VOL. XII. [NOVEMBER, 1890.] No. 8.

AMERICAN CHEMICAL JOURNAL.

Contributions from the Laboratory of Cornell University.

THE ACTION OF DILUTE NITRIC ACID ON ACETONE.

BY SPENCER B. NEWBURY AND W. R. ORNDORFF.

The action of strong nitric acid upon ketones has been studied by Chancel and others, and has been found to result in the decomposition of the ketones at the point of the carbonyl group, with the formation of fatty acids and nitro-compounds. Other powerful oxidising agents, as chromic acid and permanganates, have been shown by Wagner and Hercz to decompose acetone into carbon dioxide and acetic and formic acids. No experiments on the gradual oxidation of acetone by dilute nitric acid are recorded, and it seemed to the authors that an investigation of this action would be of interest. It is well known that Debus,[1] by the action of dilute nitric acid on alcohol, obtained glycolic and glyoxylic acids. Similarly Lubjawin[2] obtained glyoxal from aldehyde; the oxidation in both cases taking place in the methyl group. It was thought probable by the authors that similar treatment of acetone might yield products of oxidation without breaking up the molecule. This expectation was proved, however, to be unfounded, and the experiments led to results very different from those which were anticipated.

Commercial acetone, purchased from Roessler & Hasslacher, was thoroughly dried by boiling for several hours with calcium chloride, and carefully distilled through a long Hempel tube. All but a slight residue passed over between 56.4° and 56.6°.

[1] Ann. Chem. (Liebig) **100**, 1. [2] Ber. d. chem. Ges. **14**, 1713 and 2685.

1000 grams of strong nitric acid (sp. gr. 1.42) was mixed with 1200 grams of water, and the mixture allowed to become quite cold. 1000 grams of purified acetone was then added. No rise of temperature took place on the addition of the acetone. The mixture was placed in tall glass cylinders, and a few drops of fuming nitric acid introduced at the bottom of each by means of a long pipette. In a few hours bubbles of gas began to rise in the liquid; this gas was found to contain considerable quantities of carbon dioxide. The gradual evolution of gas continued steadily for several weeks. At the end of two months the reaction had nearly ceased. The liquid, which then smelled strongly of hydrocyanic acid and acetic acid, was poured into a large evaporating dish and allowed to evaporate spontaneously during the whole summer. After several months large crystals were found in the syrupy residue. These crystals were recrystallised from water, and on examination proved to consist of ammonium tetroxalate and free oxalic acid. On further evaporation of the syrupy mother-liquor and cooling the liquid by means of ice, a large quantity of crystals, the chief product of the reaction, separated out. These were extremely soluble in water, had a strong acid reaction, and showed the characteristic properties of oxy-isobutyric acid. In order to prepare the zinc salt for analysis a portion of the original syrup was boiled with zinc oxide until nearly neutralised, filtered, and the insoluble residue exhausted with boiling water. On cooling, zinc oxy-isobutyrate crystallised out, and after recrystallisation was analysed with the following results:

	Found. I.	Found. II.	Calculated for $Zn(C_4H_7O_3)_2 + 2H_2O$.
Loss of water at 110°,	11.74	11.72	11.72
Zinc,	21.37	21.32	21.17

The silver salt was prepared, and yielded the following results:

	Found. I.	Found. II.	Calculated for $AgC_4H_7O_3$.
Ag	51.14	51.14	51.18

The mother-liquor from the zinc oxy-isobutyrate, containing the zinc salts of any other acids present together with any neutral products of the reaction, was found to yield only a few drops of oily liquid on exhaustion with ether. On precipitating the zinc from the solution by hydrogen sulphide, filtering, and evaporating the filtrate, vapors of nitric acid escaped and some ammonium nitrate crystallised out. The mother-liquor was precipitated with

lead acetate, the lead salts suspended in water and decomposed with hydrogen sulphide. On evaporation to dryness a very small quantity of a crystalline acid substance was obtained, the quantity of which was, however, too small to admit of its identification.

These experiments show that in the action of dilute nitric acid on acetone, carbon dioxide, acetic acid, oxalic acid, hydrocyanic acid, and ammonium salts are produced, together with a large quantity of oxy-isobutyric acid. Neither pyruvic acid nor other products of simple oxidation without a breaking up of the acetone molecule are formed in perceptible amounts.

The liberation of hydrocyanic acid on oxidation of various organic compounds by nitric acid has often been observed. According to Hantzsch,[1] this is probably due to the reduction of nitric acid to nitrous acid, and the consequent formation of iso-nitroso compounds. These, on further oxidation, break up with the formation of iso-nitroso-methane, CH_3NOH, which spontaneously decomposes into water and hydrocyanic acid.

The formation of oxy-isobutyric acid by the action of hydrocyanic acid and hydrochloric acid on acetone was observed by Staedeler,[2] and is a well-known method of preparation of this substance. The nitrile of oxy-isobutyric acid is first formed, and then decomposed in presence of water and hydrochloric acid into ammonia and oxy-isobutyric acid.

$$\begin{array}{l} CH_3 \\ | \\ CO \\ | \\ CH_3 \end{array} + HCN = \begin{array}{l} CH_3 \\ | \\ C{<}\begin{array}{l} OH \\ CN \end{array} \\ | \\ CH_3 \end{array} \cdot \quad \begin{array}{l} CH_3 \\ | \\ C{<}\begin{array}{l} OH \\ CN \end{array} \\ | \\ CH_3 \end{array} + 2H_2O = \begin{array}{l} CH_3 \\ | \\ C{<}\begin{array}{l} OH \\ COOH \end{array} \\ | \\ CH_3 \end{array} + NH_3.$$

These reactions doubtless correctly express the formation of this product in the action of dilute nitric acid on acetone.

Laboratory of Cornell University, *Aug.* 1, 1890.

THE ACTION OF PROPIONIC ALDEHYDE ON ALCOHOLS.

By Spencer B. Newbury and M. W. Barnum.

The synthesis of acetal by heating aldehyde and alcohol together with a small quantity of glacial acetic acid, was accomplished by Geuther[3] in 1863. Subsequently Alsberg and others applied the

[1] Ann. Chem. (Liebig) **222**, 65. [2] Ibid. **111**, 320. [3] Ibid. **126**, 63; Jahresber. 1864, 495.

same reaction to other aldehydes and alcohols, and obtained a series of products similar in constitution to acetal. Among these experiments the action of propionic aldehyde on alcohols appears not to have been studied. It was therefore thought to be of interest to ascertain whether this substance will enter into combination with alcohols in the same manner as ordinary aldehydes.

1 volume propionic aldehyde, 2 volumes ethyl alcohol, and ½ volume glacial acetic acid were heated in closed flasks to 100° for twelve hours. The product was shaken repeatedly with a strong solution of calcium chloride to remove unchanged alcohol, dried, and submitted to fractional distillation. A large yield was obtained of a colorless product, possessing nearly the odor of ordinary acetal, and boiling at 122.8° under a barometric pressure of 74.4 cm. Analysis gave the following results:

	Found.		Calculated for $C_7H_{14}O_2$.
C	63.87	63.86	63.63
H	12.32	12.08	12.12
O	...	...	24.25

The vapor density, determined by Hofmann's method, was found to be as follows:

Found.	Calculated for $C_7H_{14}O_2$.
4.564	4.574

The specific gravity of the liquid at 0° was found to be 0.8825.

These results show the product to be propionic acetal, or *propylidene di-ethyl ether*, the next higher homologue of acetal, formed by the reaction,

$$\begin{array}{l} CH_3 \\ | \\ CH_2 \\ | \\ CHO \end{array} + 2C_2H_5OH = \begin{array}{l} CH_3 \\ | \\ CH_2 \\ | \\ CH(OC_2H_5)_2 \end{array} + H_2O.$$

By heating together propionic aldehyde, methyl alcohol and glacial acetic acid, *propylidene di-methyl ether* was obtained. It was found to boil at 86°–88°, and on analysis gave the following results:

	Found.	Calculated for $C_5H_{12}O_2$.
C	58.01	57.69
H	11.49	11.53
O	...	30.78

The specific gravity of the liquid at 0° is 0.8657.

Laboratory of Cornell University, *Aug.* 1, 1890.

THE ADDITION OF THE ELEMENTS OF ALCOHOL TO UNSATURATED COMPOUNDS.

I.—The Action of Alcohol on Acroleïn.

By Spencer B. Newbury and E. M. Chamot.

According to Alsberg,[1] acroleïn when heated with alcohol and glacial acetic acid yields *iso-tri-ethylin*, $CH_2-CH(OC_2H_5)-CH(OC_2H_5)_2$. Tawildaroff,[2] however, on repeating Alsberg's experiments, failed to obtain this product. The question whether an unsaturated aldehyde behaves like a saturated one, combining with two molecules of alcohol to form an acetal, or whether a further addition of alcohol takes place at the point of unsaturation, appeared of so great interest that the authors were led to study this reaction with care.

Acroleïn was prepared according to the instructions of Fischer (*Organische Präparate*, p. 30). This method was found to give a very satisfactory yield if thoroughly dehydrated glycerine and anhydrous potassium bisulphate were employed.

As described by Alsberg, 1 volume acroleïn, 3 volumes alcohol, and ½ volume glacial acetic acid were heated for eight hours at 100° in a closed flask. On distilling the product on a water-bath, alcohol and ethyl acetate passed over, and a large amount of tarry matter remained in the flask. It was found by experiment that acroleïn is completely decomposed, forming tarry products, when heated to 100° with glacial acetic acid. It is therefore evident that the reaction described by Alsberg does not take place under these conditions.

In order to avoid, if possible, the use of acetic acid, the experiment of heating ordinary aldehyde with alcohol alone was tried. To the surprise of the authors, this method was found to yield far more acetal than when glacial acetic acid was employed. 30 cc. aldehyde and 60 cc. alcohol, heated eight hours at 100° gave 38 cc. acetal (boiling from 100° to 105°), as compared with only 8 cc. when the same quantities were heated with the addition of 15 cc. glacial acetic acid.

1 volume acroleïn and 3 volumes absolute alcohol were heated for 15 hours at 100° in a closed pressure-bottle. On distillation on the water-bath, nearly the whole of the product passed over, and proved to consist of unchanged alcohol and acroleïn.

[1] Jahresber. 1864, 495.

[2] Ber. d. chem. Ges. **12**, 1487.

Heating for a longer period at lower temperature gave, however, more satisfactory results. The mixture of acroleïn and alcohol in the above proportions was kept at a temperature of 50° for five days. On shaking with a strong solution of calcium chloride nearly the whole of the product separated as an oily layer. This was dried and distilled *in vacuo*, since it proved to decompose somewhat on distillation at ordinary pressure. The purified product is a light colorless liquid, possessing a fruit-like odor, boiling at 85° under a pressure of 1.1 cm. of mercury, and at 180°–185°, with considerable decomposition, at ordinary pressure. Its specific gravity at 0° is 0.8959. It does not decolorise bromine-water, and is therefore not an unsaturated compound. Analysis of the product gave the following results:

	Found.		Calculated for $C_9H_{20}O_3$.
C	61.18	61.04	61.36
H	11.20	11.25	11.39
O	...	...	26.25

Determination of the specific gravity of the vapor by Hofmann's method in vapor of amyl alcohol gave the following result:

Found.	Calculated for $C_9H_{20}O_3$.
6.10	6.096

These results indicate that the product of the action of acroleïn on alcohol is *iso-triethylin*, or *tri-ethoxy-propane*, as stated by Alsberg. The boiling point, properties, and method of preparation of this compound are, however, different from those stated by the above author. It appears, therefore, that acroleïn combines with three molecules of alcohol, in the following manner:

$$\begin{array}{l} CH_2 \\ \| \\ CH \\ | \\ CHO \end{array} \quad \begin{array}{l} HOC_2H_5 \\ \\ HOC_2H_5 \\ \\ HOC_2H_5 \end{array} = \begin{array}{l} CH_3 \\ | \\ CHOC_2H_5 \\ | \\ CH(OC_2H_5)_2 \end{array} + H_2O.$$

This combination of alcohol with unsaturated compounds has been observed in other cases, notably in the formation of the nitrile of ethoxy-butyric acid by the action of alcohol on allyl cyanide, studied by Rinne[1] and Pinner.[2]

$$CH_2:CH.CH_2.CN + C_2H_5OH = CH_3.CH(OC_2H_5).CH_2.CN.$$

The position of the third ethoxy-group in tri-ethoxy-propane is not established. The difference between the boiling point of this

[1] Ber. d. chem. Ges. **6**, 389. [2] Ibid. **12**, 2056.

substance and that of propionic acetal (described in the foregoing paper) is, however, nearly the same as that between the boiling points of acetal and ethoxy-acetal. This fact and the ready decomposition of the substance on boiling may be taken as an indication that the third group occupies the α-position, and that the compound possesses the formula $CH_3.CH(OC_2H_5).CH(OC_2H_5)_2$ assigned to it by Alsberg.

On heating with anhydrous oxalic acid, acroleïn is formed, together with higher products showing the boiling point of ethyl oxalate.

II.—The Action of Crotonic Aldehyde on Alcohol.

By Spencer B. Newbury and W. S. Calkin.

The peculiar behavior of acroleïn with alcohol, observed by Alsberg, and described in the foregoing paper, led the authors to take up the study of the action of the next higher homologue of acroleïn, crotonic aldehyde, upon alcohol under similar conditions. The object of the investigation was to determine whether a simple acetal would result by combination with two molecules of alcohol, as in the case of saturated aldehydes, or whether a further addition of alcohol would take place at the point of unsaturation, as in the case of acroleïn.

Preparation of crotonic aldehyde.—The preparation of crotonic aldehyde by the usual methods (action of hydrochloric acid or zinc chloride on aldehyde) is a tedious and uncertain operation. The method suggested by Arthur Michael[1] for the preparation of aldol by the action of potassium carbonate on aldehyde, has, with certain modifications, led the authors to a most excellent process for the preparation of crotonic aldehyde. It was found that the dry potassium carbonate employed by Michael might with advantage be replaced by a dilute solution of the same substance, resulting in a great saving of time and increased yield of product. The method finally adopted is as follows:

10 grams of dry potassium carbonate is dissolved in 200 cc. of water and the solution cooled by standing in ice-water; 200 grams of aldehyde (prepared by distilling paraldehyde with a small amount of dilute sulphuric acid with the aid of a long Hempel tube), also cooled to zero, is gradually added to the

[1] This Journal **5**, 190.

solution of potassium carbonate. The aldehyde dissolves completely without apparent action if the solution is kept thoroughly cooled. After adding the aldehyde the bottle containing the mixture is allowed to stand four or five hours at the temperature of the room. At the end of this time the solution will be found to be slightly yellow and of a syrupy consistence. This is then exhausted three times with ether, and the ethereal extracts united and distilled on a water-bath. A syrupy residue is thus obtained, nearly equal in weight to the amount of aldehyde employed, and consisting almost wholly of aldol. The aldol may be purified by distillation *in vacuo*, but for the preparation of crotonic aldehyde it is simply necessary to distill the syrup from a flask with the aid of a long Hempel tube. Crotonic aldehyde and water pass over, with small quantities of ether and aldehyde. The crotonic aldehyde is separated from the water by addition of calcium chloride, dried, and rectified. In this manner a quantity of crotonic aldehyde equal to thirty per cent. of the aldehyde employed may be obtained in a single day.

Action of crotonic aldehyde on alcohol.—Mixtures of crotonic aldehyde and alcohol, in the proportion of one molecule of the former to three of the latter, were heated together at varying temperatures up to 100° for periods ranging from a few hours to several days. In all cases the two substances were found quite unchanged, no combination between them having taken place. No result was obtained on heating the mixture with a small amount of glacial acetic acid. The addition of zinc chloride, however, caused the combination to take place readily.

60 grams crotonic aldehyde was added to 120 grams absolute alcohol, and 30 grams dry zinc chloride dissolved in the mixture. The solution was then heated in closed bottles for six days at a temperature of 50°. At the end of this time the solution had become reddish in color, and the odor of croton aldehyde had almost wholly disappeared. The mixture was shaken with strong calcium chloride solution to remove unchanged alcohol, dried, and submitted to fractional distillation. A small quantity of a higher product was present, which decomposed on distillation and rendered the purification of the chief product difficult. This was finally obtained as a colorless liquid of pleasant fruit-like odor, boiling with slight decomposition at about 190°. Under a pressure of 15 centimeters of mercury it boils without decomposition at 88° to 90°.

On analysis the following results were obtained:

	Found.		Calculated for $C_{10}H_{22}O_3$.
C	62.84	62.96	63.16
H	11.58	11.43	11.58
O	...	...	25.26

Determination of the specific gravity of the vapor of the substance by Hofmann's method in vapor of amyl alcohol (b. p. 130°) gave the following result:

Found.		Calculated for $C_{10}H_{22}O_3$.
6.588	6.669	6.581

The specific gravity of the liquid at 0° was found to be 0.8825.

These results indicate that the substance is *tri-ethoxy-butane*, probably possessing the formula

$$CH_3.CH_2.CH(OC_2H_5).CH(OC_2H_5)_2,$$

homologous with the corresponding compound obtained in a similar manner from acroleïn. The position of the third ethoxy-group is of course uncertain. The comparatively slight difference between the boiling points of this compound and of the tri-ethoxy-propane described in the foregoing paper, together with the decomposition of both substances on boiling, may serve as a slight indication that the two compounds possess a similar constitution, and that the tri-ethoxy-butane obtained by the authors possesses the formula $CH_3.CH_2.CH(OC_2H_5).CH(OC_2H_5)_2$. It is hoped that experiments now in progress on the action of alcohol on unsaturated acids may throw further light on the position taken by the third ethoxy-group in the above reaction.

These experiments show that crotonic aldehyde enters into combination with three molecules of alcohol in the same manner as acroleïn, the combination taking place, however, far less readily than in the case of the latter substance.

Laboratory of Cornell University, *Aug.* 1, 1890.

Contributions from the Chemical Laboratory of Wesleyan University.

IV.—THE ACQUISITION OF ATMOSPHERIC NITROGEN BY PLANTS.[1]

By W. O. Atwater and C. D. Woods.

Reported by W. O. Atwater.

Until within a few years it has been the prevalent, though not universal, opinion of chemists and vegetable physiologists that the free nitrogen of the air is not assimilated by plants, and that, as the proportions of combined nitrogen in the atmosphere are so minute that the amounts which ordinary plants could absorb during their growth must be unimportant, nearly all of the nitrogen of plants is furnished to them by the soil, either from previously accumulated stores or from fertilising materials applied to it. In 1881 the writer instituted a series of experiments, which were repeated in 1882, and brought positive evidence of the acquisition of large quantities of nitrogen from the air by peas during their period of growth. The investigation was unavoidably interrupted until 1885, when four other series revealed large losses of nitrogen during germination and early growth. In the account of these later investigations it was urged that this loss of nitrogen was probably caused by microbes; that it helped to explain why previous experimenters had failed to find proof of the acquisition of atmospheric nitrogen by plants, especially legumes, but that the negative results obtained by the latter were also due to the exclusion of the action of electricity or microbes, by which the assimilation of atmospheric nitrogen might be aided.[2]

The circumstances which caused the cessation of the investigation from 1883 to 1885 were alike operative from the latter time until 1888. Meanwhile the very important investigations of Hellriegel[3] and others had confirmed those of the first and second

[1] Reprinted, with some alterations, from the Report of the Storrs (Conn.) Agricultural Experiment Station for 1889. A brief account of the experimental results was published in Bulletin No. 5 of that Station, October 1889.

[2] The results of the experiments of the first series were reported briefly at the meeting of the American Association for the Advancement of Science in 1881, those of the first and second series together were reported at the meetings of the British and the American Association for the Advancement of Science in 1884, and in detail in this Journal **6**, 365 (February, 1885). Those of series three to six were reported in this Journal **8**, 327 and 398.

[3] Hellriegel and Wilfarth, Unters. u. d. Stickstoffnahrung der Gramineen und Leguminosen, Beilageheft z. d. Zeitsch. des Vereins f. d. Rübenzucker-Industrie d. D. R., Nov. 1888.

series referred to, and while bringing additional evidence of the acquisition of atmospheric nitrogen, had also indicated the very strong probability that micro-organisms are active agents in the assimilation of nitrogen.

The experiments herein described are a continuation of the previous ones in this place. The methods are also similar, save that the introduction of soil infusions and observations on root tubercles were suggested by the experience of Hellriegel.

The specific question for study in the first series of experiments here was:

(1) May plants (peas), grown under normal conditions acquire any considerable amount of nitrogen, free or combined, from the air?

The second series was planned to verify the strongly affirmative results of the first and to include the collateral inquiry:

(2) How is the acquisition of nitrogen from the air affected by abnormal conditions of growth?

In the present investigation the study of the first question is continued with peas and other plants, legumes and cereals, and the two further questions have been included:

(3) What effect has the addition of soil infusions upon the formation of root tubercles under the conditions of the experiments?

(4) Is there a definite relation between the quantity or number of root tubercles and the quantity of atmospheric nitrogen obtained by the plant?

Previous Experiments in Middletown.

Before entering upon the details of the work to be reported herewith, a recapitulation of the experiments of the first two series above referred to may be appropriate. The plan of the experiments was similar to that of the ones to be reported beyond. The plants were grown in purified sand, supplied with solutions of appropriate salts including nitrogen and nitrates, and kept in open air, but protected from rain and dew. The first series included five, and the second, twelve experiments. The figures of numbers five to twelve of the second series given in the table herewith will, with the explanation quoted, suffice to illustrate the results obtained.

The "concentrated" solutions contained from 2.5 to 6, and the

"dilute" from 0.3 to 1.6 parts of water-free salts in 1000. A concentration of 1 per 1000 has elsewhere been found favorable, and one of over 2 per 1000 unfavorable to normal assimilation.[1]

The well-fed plants had quantities of mineral food estimated to be sufficient for their nourishment, the scantily-fed ones, one-half as much. The "larger nitrogen ration" was estimated to supply an amount of nitrogen rather small in proportion to the mineral food, and the "smaller nitrogen ration" less than one-half as much as the larger. The gain or loss of nitrogen is computed by adding to the amount of nitrogen in the plants the amount left in the nutritive solution at the end of the experiment, and subtracting from their sum the sum of the amounts in the seed and in the nutritive solution at the start. The figures for "apparent gain or loss" represent, therefore, the quantities acquired from the air less whatever may have been liberated from solution or seed or plants during growth.

Statistics of Experiments on the Assimilation of Atmospheric Nitrogen by Peas.

Conditions of Experiments.			No. of Experiments.	Nitrogen Supplied.			Nitrogen found at End of Experiment.			Apparent Gain + or Loss — of Nit'g'n.
				In Seeds.	In Nutritive Sol'n.	Total.	In Plants.	In Resid. Sol'n.	Total	
				Mg.	Mg.	Mg.	Mg.	Mg.	Mg.	Mg.
Larger Nitrogen Ration.	Concentrated Solution,	Scantily fed,	3	70.3	136.9	207.2	197.5	12.7	210.2	+ 3.0
		Well fed,	6	34.8	136.9	171.7	149.6	1.2	150.8	— 20.9
	Dilute Solution,	Scantily fed,	12	68.8	136.9	205.7	260.2	45.7	305.9	+ 100.2
		Well fed,	10	34.6	136.9	171.5	277.8	35.7	313.5	+ 142.0
Smaller Nitrogen Ration.	Concentrated Solution,	Scantily fed,	7	71.5	59.4	130.9	158.1	0.0	158.1	+ 27.2
		Well fed,	5	34.2	59.4	93.6	156.1	0.0	156.1	+ 62.5
	Dilute Solution,	Scantily fed,	11	72.5	59.4	131.9	210.9	2.7	213.6	+ 81.7
		Well fed,	9	35.3	59.4	94.7	186.5	1.4	187.9	+ 93.2

The following statements are from the summary of the conclusions, which embodies also those of the four series of experiments on the liberation of nitrogen during germination and the early growth of peas above referred to as undertaken in connection with this investigation:

1. "The experiments showed in some cases a large acquisition of nitrogen from the air, the gain amounting in some instances to half or more than half of the whole nitrogen in the plants.

[1] We have found plants to grow well in more concentrated solutions (see also Hellriegel, Naturwiss. Grundlagen des Ackerbaus), but in these experiments, at any rate, there was less apparent gain of nitrogen with the concentrated than with the dilute solutions.

In other cases there was, apparently, a very small gain or a loss of nitrogen. There seems to be excellent ground for assuming that the cases in which either only a small gain or a loss of nitrogen was observed (in all of which the conditions of growth were abnormal) are to be explained by the escape of nitrogen either from the nitrates of the nutritive solution or from the seeds during germination, or from the growing plants. The proof of the acquisition of atmospheric nitrogen which is furnished by the cases in which the conditions of growth were normal, in each of which the amount acquired was large, is thus rendered the more emphatic. The faculty of obtaining nitrogen from the air appears to be especially characteristic of the legumes. By what species of legumes or other families of plants it is possessed, it is as yet impossible to say.

2. "The liberation of nitrogen appears to be due, in some cases if not in all, to ferments. To explain why it should take place in one case and not in another, is as difficult as to account for the fact that zymotic diseases attack one animal and not another, or that the plants of certain fields are affected by fungi, while others escape. It is, however, noticeable, that in nearly all the experiments in which no gain of nitrogen has been observed, the plants have been ill fed, or the nutritive solutions have been very concentrated, or other conditions have been abnormal; while, so far as the details at hand show, the largest gains have been found in the cases where the conditions of growth were most favorable.

3. "How the nitrogen was obtained in the experiments in which its acquisition is proven, is still a matter of doubt. It must have been taken either as free or as combined nitrogen, and either directly through the foliage or indirectly through the soil and nutritive solutions and the roots of the plants.

4. "It would be going too far positively to assume that in the experiments which have given the strongest evidence against the fixation of free nitrogen by plants—namely, those of Boussingault and of Lawes, Gilbert and Pugh, in which the plants were raised under glass, in confined air, or in air washed free from nitrogen compounds—the negative results are due to the escape of nitrogen in the manner above suggested, though such liberation cannot be regarded as impossible. But it is at least conceivable that the measures adopted to exclude nitrogen compounds—keeping the plants under glass and passing the air through acid and alkali

solutions before entering—may have excluded the action of electricity or of microbes, by which the fixation of free nitrogen may perhaps be effected. The plants were also, for the most part, very poorly fed. That this may be the cause of deficient assimilation of nitrogen is indicated by the experiments with peas above referred to. At any rate, until we know more about the relations of electricity and of micro-organisms to the fixation of nitrogen, we can hardly be warranted in assuming that these experiments prove that plants grown under normal conditions do not assimilate the free nitrogen of the air.

5. "To what extent the attested acquisition of atmospheric nitrogen is a function of the plant alone; in how far it may be dependent upon the action of electricity, microbes, or other agency induced by the plant; by what species of plants and under what conditions it is accomplished, are of course matters for further study. The experiments of Berthelot imply that organic matter, through the agency of electricity, and soils containing clay, through the agency of living organisms, may fix the free nitrogen of the air. It may, hence, be inferred that in some of the experiments in which acquisition has been observed, the nitrogen may have been first taken from the air by the medium in which the roots grew and communicated through the latter to the plants. But in my experiments this medium consisted of ignited sea sand and an aqueous solution of salts. I am aware of no observed facts to imply that these, separately or together, are able to fix free nitrogen by aid of electricity, micro-organisms, or any other means. In the present state of our knowledge, therefore, the balance of probability seems to decidedly favor the assumption that the plants themselves must be factors in the acquisition of atmospheric nitrogen.

6. "Messrs. Lawes, Gilbert, and Warrington have shown the great probability that the legumes, which appear to possess in high degree the power of obtaining nitrogen from natural sources, induce the action of nitrifying ferments by which the inert nitrogen of the soil is made available. It is equally conceivable that the same plants and others may favor the action of nitrogen-fixing micro-organisms."[1]

[1] See, however, later views and experiments by Messrs. Lawes and Gilbert, Phil. Trans. 1889, 1, and especially Proc. Roy. Soc. **47** (1890), 85.

Plan of the Experiments here Reported.

The plants in the experiments here described were all grown in purified sea sand. A number of trials were made by water culture, and two (with corn) in ordinary garden soil. A difficulty with the last is that no method which we have as yet been able to find for the determination of nitrogen will admit of its estimation with the desired accuracy in the large amount of soil needed for satisfactory development of the roots.

Effort has been made to grow the plants under conditions as nearly normal as is consistent with a rigid control over the supply of nitrogen. To this end an abundance of plant food (nitrogen excepted) in not too concentrated solutions, room for the development of roots, exposure to sun and air, and protection from wind, rain, dew and excessive heat, have been provided.

An exact account of all nitrogen supplied the plants, aside from that brought to them by the air, was kept, and at the end of the experiment the nitrogen in the whole plant, as well as that left unused in the nutritive solution, was determined. The difference between these two amounts must show the loss or gain in nitrogen. A loss must indicate decomposition either of the organic nitrogen of the seed or plants or of the nitric acid of the nitrates fed, or of both. A gain must represent nitrogen acquired from the air in excess of any lost either from the organic matter of the seed or plant, or from the nitrates of the food.

Appliances, Materials, and Methods.

Shelter.—In lack of a satisfactory greenhouse, a temporary structure was built with board walls and "three-quarters" roof. The board walls were five feet high at the front and side and higher at the back. At the front and sides the boards were hinged so as to open conveniently. The end gable walls were of canvas, buttoned like an ordinary carriage curtain. The canvas roof opened and closed with a roller, somewhat like an ordinary roll awning. The roof is steep and has usually proved an ample protection from the rain, though in a long-continued storm the past autumn the rain beat into part of the house so as seriously to interfere with one series of experiments. The canvas had become somewhat worn from use; it is doubtful if the accident would have occurred with new canvas. The house is easy to manage;

two minutes are sufficient in which to close and thoroughly secure it at night or before a storm, and still less time is needed to open it.

By this arrangement the plants are grown in the open air in pleasant weather and protected from rain and dew by being kept under cover at night and in rainy weather. In the few cases when the sun's heat was excessive the roof was closed, leaving the sides open. The white canvas allows considerable light to penetrate and more or less air to circulate at all times, and the plants have not suffered materially even when, as occurred more than once during the past summer, it was necessary to keep the house closed for several days at a time. The extreme humidity of the atmosphere, which caused the plants to become "drawn" or young plants to "damp off," in gardeners' phrase, is the greatest drawback we have found, and this seemed to be due more to the extraordinary wetness of the past season than to the kind of house employed. Of course it is not such an arrangement as is to be desired, and more satisfactory results are expected in a greenhouse, which it is hoped may be built for the purpose.

Pots.—For pots in which to grow the plants, ordinary glass bottles with their bottoms cut off, or bell jars with open tops, varying in capacity from one to twenty liters, were employed. They were turned neck downwards, a watch-glass was placed over the neck of each and the sand poured in until they were filled within one or two centimeters of the top. Moistening the sand before putting into the jar to avoid too close packing has not been found necessary in our experiments. A glass beaker was placed under the mouth of each pot to catch any solution or sand that might run through. This simple and inexpensive arrangement has served its purpose most satisfactorily. The drainage insures against excess of water and provides circulation of air without the use of glass, pebbles, cotton, tube for conveying air to the bottom, or other arrangements that have been recommended for the purpose.[1] The pots were enclosed in wooden boxes so constructed as to afford easy access by a door in the side. In our earlier experiments each pot was placed in a box by itself[2]; in the later work it has been found less expensive and more convenient to put a number of pots, sometimes twelve or more, in one box.

Soil.—Sea sand was freed from coarse particles by sifting,

[1] See Hellriegel, Naturwiss. Grundlagen des Ackerbaus, S. 767. [2] This Journal 6, 367.

thoroughly washed with water, and ignited at a red heat for some time. The sand thus treated gave, in repeated tests, no trace of nitrogen by either the soda-lime or the Kjeldahl method.

Food Supply.—The mineral elements needed for the growth of the plants were added in amounts to make one part or less by weight of dissolved salts in one thousand parts of the solution. Some of the plants received no combined nitrogen except that in the seed; to others nitrates were added, but in such small quantities that the minerals were relatively in excess; to others enough nitrogen was added to make the mixture of plant food correspond more nearly to the composition of the plants.

Seed.—Seeds were selected of normal appearance and as uniform in size and weight as practicable. After weighing, each seed was wrapped in filter paper, moistened and allowed to germinate. When the radicles were a centimeter in length or thereabouts, such seeds as germinated well were selected for planting.

Soil Infusions.—The soil infusions were prepared by treating 300 grams of soil taken from near the roots of vigorous plants, with 750 cc. of hydrant water for 24 to 48 hours, with occasional shaking. The liquid decanted with the least possible sediment constituted the "soil infusion." The maximum amount of nitrogen found by analysis in 25 cc. of soil infusion was 0.4 mg.; the minimum, 0.06 mg.; and the average of 21 analyses of seven kinds of soil infusion gave 0.26 mg. of nitrogen. This amount is so very small that no account is made of it in the statements of nitrogen supplied.

Water.—The water used in these experiments was prepared by distilling well-water, which contained only minute traces of free ammonia and very little so-called albuminoid nitrogen, with the addition of sodium hydroxide and potassium permanganate. The distillate was rejected until Nessler's reagent produced no appreciable coloration. This so-called "nitrogen-free" water actually contained a minute trace of ammonia, the average of several determinations giving 0.0066 milligram of nitrogen in one liter of water. In only two of the experiments with plants were more than twenty liters of water used, and as 150 liters would, by the determinations above cited, contain only one milligram of combined nitrogen, error from the use of this water is too small to be taken into account.

Nutritive Solutions.—Four different nutritive solutions were employed. All were so prepared as to contain one part by weight of salts to one hundred parts of solution, the proportions being made as accurate as practicable by the use of chemically pure salts. In those containing nitrogen, determinations of the latter were made. The solutions were:—

Phosphoric Acid Solution.—This consisted of primary potassium phosphate (KH_2PO_4) dissolved in water in the ratio of 1 gram to 100 cc. 1 cc. contained about 5.2 milligrams P_2O_5 and 3.5 milligrams K_2O.

Magnesium Solution.—Magnesium sulphate ($MgSO_4$) in water, 1:100. 1 cc. contained 3.8 milligrams MgO and 6.7 milligrams SO_3.

Iron Solution.—Ferric chloride (Fe_2Cl_6) in water, 1:100. 1 cc. contained 3.4 milligrams Fe and 6.6 milligrams Cl.

Nitrogen (N III) Solution.—Calcium nitrate ($Ca(NO_3)_2$) and potassium nitrate (KNO_3). 1 part of each salt or two of both together to 200 parts water. 1 cc. contained approximately 1.54 milligrams nitrogen and 1.7 milligrams CaO. The "N III" solution was always supplied to the plants from the same 25 cc. pipette, which actually delivered at 16° C., 24.895 cc. The mean of several analyses gave 37.66 milligrams of nitrogen in this quantity of the nitrogen solution used in 1888, and 37.94 milligrams in that of 1889.

When the solutions were applied, enough water was added to make the solution in the sand contain less than one part of salt to one thousand parts of water.

Preparation for Analysis.—At the end of the experiment the aërial portions of the plant were harvested and the roots separated from the sand by washing with water. The separation is easily effected, and but comparatively little water is required if the harvesting is done before the plants are too much withered and the washing follows before the roots are dried. The nitrates of the "residual solution" are first removed with water. The washings are evaporated for the determination of nitrogen in the residual solution. After the nitrates are supposed to be completely washed out, another extraction is made in each case, and the water evaporated and tested for nitrates by the same quantitative method as for the regular determination. The pots serve conveniently as funnels, and, as repeated tests have shown, but a

comparatively small amount of water is needed to wash out the nitrates completely. The pots are then supported obliquely with the surface downwards and the sand washed out by a stream of water. The roots, which suffer very little loss in this process, are dried and the nitrogen is determined in them as in the tops.

Estimation of Number of Root Tubercles.—The tubercles vary from the size of a pin head to that of a small pea, or larger, and tend to grow together in masses, so that it is practically impossible to count them, and even if counted, the number would mean but little for purposes of comparison because of the variations in size. An arbitrary estimate of their amount was, however, made at the time of the separation of the roots from the sand by washing. As this, of course, preceded the weighings and analyses, the observer was free from bias in judging of the abundance of the tubercles. When the number was so small that they could be readily counted, the roots were spoken of as having "few tubercles"; more than could be readily counted were spoken of as a "fair number," or, when they were present in great abundance, the expression "a large number" was used. The estimates are relative and depend somewhat upon the amount of roots, for what would be a large number with a small root development would be a "fair number" when distributed over a large amount of roots. This arbitrary classification, which presented but little difficulty in practice, is used in the descriptions and tables beyond.

Methods of Analysis.

Details of analyses are given in the Appendix beyond. The methods used were as follows:

Nitrogen in Seeds.—A considerable quantity of the seed was ground, and samples from it analysed by either the soda-lime or the Kjeldahl method, or both. The average of these analyses was assumed to represent the percentage of nitrogen in the seeds of the same lot which were sown in the experiment.

Nitrogen in Plants.—In the earlier work the analysis of the plants was made by grinding and estimating nitrogen by the soda-lime method, in samples of the whole and multiplying in the usual way. In the experiments here described, unless the plants weighed more than twenty-five or thirty grams, they were put into one or more Kjeldahl digesting flasks and treated directly without grinding. In an ordinary digester no difficulty was found

in handling ten grams, and as much as twenty grams have been successfully used. The only trouble is from frothing, which can be prevented by slow heating. After digesting, the solution was diluted and divided into aliquot parts for distilling, each portion being distilled and titrated by itself. By thus determining the nitrogen in the entire sample, the labor was reduced, and as no sampling was necessary, the accuracy was increased. Usually the whole solution was diluted to 300 cc. and one-third taken for each determination. For convenience in calculating, the amounts of alkali used for the back titration in each portion from one experiment were added together and their sum subtracted from the cc. of alkali solution corresponding to the total number of cc. of acid used. In this way the total nitrogen was determined, but the details of each part of the analysis were not kept distinct; hence the analytical details would only show the total amount of nitrogen found in the entire plant of a given experiment. As the chief use of details in the Appendix is to show the numbers and comparisons of determinations, the details of the determinations of the nitrogen in the plants are not given there. It may be added, however, that the triplicate determinations agreed very closely, as would be expected from the fact that the method was the same as that used for the determination of nitrogen in the seeds, of which details are given.

Nitrogen in Nutritive Solutions.—The nitrogen in the nutritive solutions and in the residual solutions extracted from the sand at the end of the experiment was determined by the method of Schulze-Tiemann. Properly manipulated this method gives very accurate results, as is shown by an investigation of the method and its sources of error, the results of which will be printed in detail elsewhere.

Notes on the Culture and the Growth of the Plants.

Like other experimenters, we have found it feasible, with proper care, to grow plants in sand culture to compare favorably with the same varieties of plants grown in the field or garden. Different species of plants require somewhat different treatment, which can be learned only by experience. On the whole our plants have succeeded better in cool than in hot weather, perhaps because of the difficulty of keeping the soil (sand) cool when the weather is hot. The tendency of peas, especially young vines, to mildew in hot,

damp weather has been very troublesome. In a long-continued wet period last July over fifty young pea plants "damped off." Numerous drawbacks of this and similar kinds have been experienced. Of 267 experiments undertaken only about 100 have proven wholly successful. Still we deem sand culture decidedly practicable and useful for the plants we have worked with.

East Hartford Early Peas.—This is an early, dwarf variety prized by market gardeners in this vicinity. In ordinary culture the vines grow from two and one-half to three feet in height and in rich soil are somewhat taller. In our experiments many of the plants attained the normal size and some were unusually large. In numerous cases peculiarities of growth demand attention. Although these peculiarities were no more marked in the plants without than in those with nitrogen in the food supplied, it will be well for convenience to consider especially the plants that were not fed with nitrogen aside from that contained in the seed. Usually the growth of these plants was reasonably uniform and apparently normal until they attained a height of twelve or fifteen inches. From this stage one of three things happened, leading to the following classification:

(1) A "starvation" period, analogous to that described by Hellriegel,[1] began, in which the healthy green color of the leaves gave place to a sickly yellow, the plants blossomed and developed small and imperfect peas or none at all, and then died. The plants manifesting this demeanor had very few, or, more commonly, no root tubercles. Experiment No. 137[2] illustrates this. Three seeds, weighing together 0.96 gram, gave rise to two plants fifteen inches in height, and one, ten inches in height and bearing one pod containing one pea. The dry plants weighed 0.97 gram and contained 11 milligrams less nitrogen than was contained in the seed. There were no root tubercles.

Sometimes the plants recovered from this starvation stage and developed so as to be grouped with those of the other classes.

(2) The plants retained their healthy appearance, blossomed, developed a few seeds, rarely more than one or two, and then died without attaining a greater growth. Root tubercles were usually found in greater or less abundance in this class. Experiment No. 119 is a case in point. Two seeds, weighing 0.53 gram, gave rise to two plants 18 inches high, bearing three pods and 3 peas. The

[1] Hellriegel und Wilfarth, loc. cit.

[2] See tables at end of this article.

dry plant weighed 1.57 grams and contained 31 milligrams more nitrogen than was in the seed used. There were a large number of root tubercles.

(3) Other plants kept on growing, were apparently normal, and frequently attained a height of four or more feet before blossoming. Usually these plants bore a fair number of perfect seeds.

In the experiments with East Hartford Early peas, from two to five plants were grown in a single pot, but in no case did all of the plants of an experiment attain this large growth. Thus Experiment No. 136 had four plants, of which three might be reckoned with the second, and one with the third class. Four seeds, weighing 0.94 gram, gave rise to three plants 14 inches high bearing three pods and containing three peas, and one plant 58 inches in height bearing two pods and nine peas. The first three plants were ripe July 1st; the other kept on growing till August 15th. The four plants weighed 7.06 grams and contained 243 milligrams more nitrogen than was in the seed used. Root tubercles were abundant.

Examples of all three of these phases of growth sometimes occurred in the same pot. As a rule, the larger the plant the greater was the number of root tubercles found upon it.

The last two phases of growth were even more noticeable in the experiments in which nitrates were supplied to the plants. Occasionally the first, or starved form, appeared. Usually the plants were relatively taller and contained higher percentages of nitrogen than those not fed with nitrates. In several cases these so-called "dwarf peas" attained a height of over eight feet.

Experiment No. 148 illustrates all three phases of growth in a case in which nitrogen was supplied in nitrates. Four seeds gave rise to four plants, 16, 35, 42 and 83 inches high respectively. The last plant had 11 peas, the other three 13. In this case tubercles were abundant on the large plants.

Champion of England Peas.—As a rule these peas grew much more uniformly than the dwarf peas, though in a single pot they often varied two or more feet in height. The different phases of growth were less marked than with the dwarf peas.

Alfalfa.—We have found but little difficulty in growing alfalfa in sand; even plants not fed with nitrogen, but supplied with plenty of mineral food, have developed normally and have at no time shown any very marked starvation-stage of growth. Two

experiments will illustrate the vigor of growth, both with and without a supply of nitrogen in the food.

In Experiment No. 109, three plants, to which no nitrogen was fed other than the small fraction of a milligram contained in the seed and soil infusion, had sixteen branches averaging 15 inches in height, and weighed, air dry, 3.22 grams. They obtained from the atmosphere 137 milligrams of nitrogen.

In Experiment No. 113, one plant fed with nitrogen in the form of nitrates, had 35 branches, averaging 20 inches in height; weighed 12.9 grams and contained when mature 382 milligrams of nitrogen more than was supplied to it in seed and nutritive solution.

Oats and Corn.—Oats grew well, better than field oats average in this climate. The corn grew fairly well, but did not fruit fully. Lack of fertilisation from insufficiency of pollen seemed to be the chief trouble. Owing to its tendency to great root development, pots of three to five gallons capacity were used.

The Experiments here Reported.

The experiments here described may be divided into the following series:

Series.	Year.	Kind of Plants.	No. of Exp'ts.	No. of Plants.
VII	1888	Champion of England Peas	25	64
VIII	1888–89	Alfalfa	5	9
IX	1888	Corn	8	15
X	1889	East Hartford Early Peas	34	104
XI	1889	Champion of England Peas	16	70
XII	1889	Oats	11	66
XIII	1889	Corn	18	35
		Total	117	363

Specimen Experiments.

The methods may be illustrated by a description of two typical experiments.

Experiment No. 135, with East Hartford Early Peas, Series of 1889.—The pot used in this experiment held 3 kilograms (six and a half pounds) of sand. This was placed in the pot April 10th, and the same day four well-sprouted peas, which had weighed before sprouting 0.998 gram, were planted. When planted they were fed with mineral salts, without combined nitrogen, in such

amount that the ratio of salts to water was about 1 to 1500. They were again fed with minerals on May 10th. During the period of growth, water was given them 41 times, 6.6 liters being used. No soil infusion was given.

About the middle of June two of the plants had stopped growing. These were not more than one foot in height, and when harvested were found to have no root tubercles. The other two kept growing, though not equally well, till about July 9th, when they were harvested. At this time one of the plants was two and one-half and the other a little over five feet in height. Both had root tubercles. The four plants had 9 pods and 15 peas. The weight of the partly-dried fruit and vines was 7.97 grams. The roots, freed as far as practicable from sand, weighed 1.27 grams, making the total weight of the four plants 9.24 grams. The plant altogether contained 237.1 milligrams of nitrogen. The seed, as shown by analysis of similar ones, contained 39.9 milligrams of nitrogen. The balance-sheet of the experiment is as follows:

Nitrogen fed in the seed, . . .	39.9 milligrams.
Nitrogen found in plants, . . .	237.1 milligrams.
Gain, ...	197.2 milligrams.

The gain of nitrogen during the growth was thus 197.2 milligrams.

In a large number of experiments the plants have had no root tubercles. In nearly every case of this sort there has been more or less loss, instead of gain, of nitrogen. The natural inference is, that in the experiment just described all the gain of nitrogen was made by the larger plants which had the root tubercles, and that they thus actually acquired from the air not only 197.2 milligrams of nitrogen which is counted as gain, but enough besides to offset more or less loss where there were no tubercles.

Experiment No. 165, *with Champion of England Peas.*—Six kilograms of sand were placed in the pot April 15th, and the same day six peas, weighing 2.3 grams, were planted. The plants were fed with minerals and with nitrogen in the form of calcium and potassium nitrates, when the seeds were planted, and on May 15th, June 20th, and June 22d. On May 11th and 20th, 25 cc. of an infusion of garden soil in which peas were growing, were added. During the whole period of growth the plants were watered 46 times, 13.9 liters water being used. The plants had finished their

growth and were nearly ripe on July 9th, when they were harvested. The notes taken at the harvesting were as follows:

Six Plants Grown in Sand.

HEIGHT.	NO. OF PODS AND PEAS. Pods.	Peas.
3 feet 8 inches	1	2
4 " 9 "	3	5
5 " 10 "	4	7
4 " 0 "	2	6
5 " 9 "	3	7
5 " 6 "	2	7
Total	15	34

The roots had a large number of tubercles, which were pretty evenly distributed. The partly dried vines and fruit weighed 24.85 grams, the roots, freed from sand as completely as practicable, 7.87 grams, making the total weight of the six plants 32.72 grams. These contained 694.5 milligrams of nitrogen. The soil (sand) at the end of the experiment contained 23.5 milligrams of nitrogen as nitrate. The balance-sheet is as follows:

Nitrogen fed in the seed, .	105.1 mg.	
Nitrogen fed in solution, .	447.7 mg.	
		552.8 mg.
Nitrogen found in soil, .	23.5 mg.	
Nitrogen found in plants, .	694.5 mg.	
		718.0 mg.
Gain in nitrogen, ...		165.2 mg.

The principal statistics of the experiments are given in the tables at the end of this article.

Absorption of Combined Nitrogen from the Air.

Tests made in connection with previous experiments here failed to give indications of any considerable absorption of ammonia or nitric acid by nutritive solutions in sand exposed to the air under conditions similar to those of the experiment, and implied that no considerable quantities of combined nitrogen from the air could have been purveyed to the plants by the solutions.[1] As a further

[1] The following is from the discussion of the experiments referred to: "During the course of the experiments of the second series, a number of pots with sand and solutions like those in which the plants grew were kept alongside the latter. The solutions at the end of the experiments revealed only such minute quantities of combined nitrogen as are commonly found in natural waters exposed to the air. That these solutions, without plants, had so little of nitrogen compounds is, however, no proof that the solutions in which the plants grew might not

precaution the following tests were made in connection with the experiments here reported. Pots were filled with sand, and nutritive solutions (see descriptions of nutritive solutions above) were added as in the regular experiments, but no seeds were sown. In two cases dilute acid was used instead of the nutritive solutions. They were put into the planthouse, July 11th, and brought to the laboratory for analysis, October 20th, 1889, and were thus exposed for over three months to the same atmospheric conditions as those in which the plants were grown. They were watered often enough to keep the sand apparently as moist as that in which the plants were grown, 1100 cc. of water being used for each pot. Eight such tests were made, in four series, as follows:

A. With Dilute Sulphuric Acid.—Two pots, Nos. 65 and 66, each holding 1½ kg. of sand, were each supplied with 10 cc. of dilute sulphuric acid containing, approximately, 30 mg. of H_2SO_4 in 1 cc. At the end of the trial the solutions were extracted and tested for ammonia and nitric acid. Each gave by distillation and titration approximately one milligram of ammonia and no trace of nitric acid by the Tiemann-Schulze method, thus indicating that a minute quantity of ammonia and no appreciable amount of nitric (or nitrous) acid had been absorbed from the air and fixed by the acid solution.

B. With Nutritive Solutions containing no Nitrates.—Two pots, Nos. 67 and 68, each holding 1½ kg. of sand, were each supplied with 15 cc. phosphoric acid solution, 10 cc. of the magnesium solution and 1 cc. of the iron solution used in the experiments. Extracted and tested as above, at the end of the trial neither yielded any appreciable quantity of ammonia or nitric acid.

C. With Nutritive Solutions, including Nitrates.—Two pots, Nos. 69 and 70, each holding 1½ kg. of sand, received each 15 cc. of the phosphoric acid solution, 10 cc. of magnesium solution, 1 cc. of the iron solution, and 25 cc. N.III solution (calcium and potassium nitrates), used for the experiments. At the end of the trial both were extracted and tested, as was done with the previous series. In neither was any appreciable quantity of ammonia found. Each had received 37.66 mg. of nitrogen in the "N.III" solution.

have yielded to the plants some of the ammonia which they were continually absorbing, and which, if not somehow seized upon, would escape by virtue of its tension. The fact that the solutions in which the plants grew were neutral or faintly alkaline, would, however, make the hypothesis of any considerable absorption of ammonia apparently improbable. It is worth noting, too, that the residual solutions at the end of the experiment contained only the minutest quantities of ammonia discernible by aid of Nessler's reagent."—This Journal **6**, 376.

No. 69 gave 36.66 and No. 70, 36.30 mg. of nitrogen, as nitric acid or other nitrogen compound, by the Tiemann-Schulze method. There was, then, no indication of absorption of ammonia, but very small quantities of nitrates were lost.

D. With Nutritive Solutions, including Nitrates and Pea-Soil Infusion.—Two pots, Nos. 71 and 72, each holding 2 kg. of sand, received each 15 cc. of phosphoric acid solution, 10 cc. magnesium solution, 1 cc. iron solution, 25 cc. N.III solution and 25 cc. of pea-soil infusion. At the end of the trial neither gave any appreciable quantity of ammonia. Each had received 37.66 mg. of nitrogen in nitrates. In No. 70, 36.30, and 71, 36.84 mg. of nitrogen was obtained by the Tiemann-Schulze method. The results were, therefore, essentially the same as those in series C.

It appears, then, that no considerable amount of combined nitrogen was acquired either by the nutritive solutions or by an acid solution in sand under the conditions in which the plants of the experiments were grown. Of course the solutions in which the plants grew were subject to changes different from those to which the solutions in these blank trials were exposed, but it is difficult to conceive how either the sand or the solutions in which the plants grew, or the sand and solutions together, could have absorbed and yielded to the plants more combined nitrogen, either in the form of ammonia, nitrates or otherwise, than would be acquired by the nutritive solutions or a dilute acid solution without plants but otherwise subject to the same conditions.

The natural inferences are that:

(1) No considerable quantity of combined nitrogen was derived from the air and yielded to the plant by the medium in which the plant grew.

(2) The slight loss of nitrates may possibly indicate decomposition, but it is small, varying from 0.8 to 1.3 milligrams, and may very likely be due, in part at least, to experimental errors.

Discussion of Results of Experiments.

The principal statistics of the experiments are collated in the tables in the Appendix to this article, and may be summarised as in Tables 1, 2, 3, 4 and 5, which follow here.

As previously explained, the estimates of the numbers of tubercles were made before the analysis of the plants, and thus the observer was free from bias.

While it is not practicable to give more than a relative idea of

their abundance, this grouping into few, fair number, and large number, presented but little difficulty.

TABLE 1.

Experiments with Oats, Series XII, 1889.

SUMMARY OF RESULTS.

	No. of Experiments.	No. of Plants in Experiments.	Average Gain (or Loss —) of Nitrogen.
			Mg.
Not fed nitrogen except in seed	4	24	2.3
Fed 304 milligrams nitrogen as calcium and potassium nitrates	3	18	—101.5
Fed 607 milligrams nitrogen as calcium and potassium nitrates	3	18	—207.8
Total	10	60	

Table 1 epitomises the results with oats. The experiments are arranged in accordance with the amounts of combined nitrogen fed. No tubercles were found upon the roots. It will be noticed that plants not fed with nitrates made a very slight gain (the largest gain was 3.1 and the smallest 1.6 milligrams), while in each case where nitrates were supplied there was a considerable loss, and that the loss increased with the amount of nitrates added. Doubling the nitrogen fed doubled the loss of nitrogen.

TABLE 2.

Experiments with Corn, 1888–1889.

SUMMARY OF RESULTS.

	No. of Experiments.	No. of Plants in Experiments.	Average Gain (or Loss —) of Nitrogen.
			Mg.
Not fed nitrogen except in seed, Series IX, 1888	4	7	5.6
Not fed nitrogen except in seed, Series XIII, 1889	6	12	9.5
Fed 114 milligrams nitrogen as nitrates, Series IX, 1888	4	8	15.6
Fed 607 milligrams nitrogen as nitrates, Series XIII, 1889	6	11	— 88.4
Fed 1518 milligrams nitrogen as nitrates, Series XIII, 1889	6	12	—236.8
Total	26	50	

Table 2 epitomises the results with corn. The experiments are arranged in accordance with the amount of combined nitrogen fed. No tubercles were found upon the roots. It will be noticed that plants not fed with nitrates, and those fed with the smallest proportion of nitrates made a very slight gain, while in the other cases where nitrates were supplied, there was a considerable loss, and that the loss increased with the amount of nitrates added.

TABLE 3.

Experiments with Alfalfa, Series VIII, 1888–1889.

SUMMARY OF RESULTS.

	Root Tubercles.	No. of Experiments.	No. of Plants in Experiments.	Average Gain of Nitrogen.
				Mg.
Not fed with nitrogen except that in seed	None	..	..	..
	Few	..	..	..
	Fair number	1	3	137.5
	Large number	..	..	..
	Total	1	3	
Fed with 340 milligrams nitrogen as calcium and potassium nitrates	None	..	..	..
	Few	3	4	84.0
	Fair number	..	..	..
	Large number	1	1	382.2
	Total	4	5	

Table 3 summarises the results with alfalfa. As explained in Table 10 beyond, the plants made but little growth the first season and a number died. Those which survived made a very satisfactory growth the second season. All the plants had root tubercles.

TABLE 4.

Experiments with Peas.

SUMMARY OF RESULTS.

	Root Tubercles.	No. of Experiments.	No. of Plants in Experiments.	Average Gain (or Loss —) of Nitrogen.
				Mg.
CHAMPION OF ENGLAND PEAS. *Series* VII, 1888.				
Not fed with nitrogen except that in seed	None	6	13	—9.8
	Few	1	3	—1.7
	Fair number	1	3	85.6
	Large number	1	3	116.7
	Total	9	22	
Fed with 76 to 252 milligrams nitrogen as calcium and potassium nitrates in addition to that in seed	None	6	13	—22.7
	Few	4	11	— 3.1
	Fair number	3	9	19.7
	Large number	3	9	49.0
	Total	16	42	
Series XI, 1889.				
Not fed with nitrogen except that in seed	None	2	6	— 9.0
	Few	1	4	—13.5
	Fair number	2	8	69.4
	Large number	1	4	78.7
	Total	6	22	
Fed with 152 to 448 milligrams nitrogen as calcium and potassium nitrates in addition to that in seed	None	..	..	..
	Few	2	10	26.5
	Fair number	1	4	60.2
	Large number	7	34	149.6
	Total	10	48	
EAST HARTFORD EARLY PEAS. *Series* X, 1889.				
Not fed with nitrogen except that in seed	None	2	4	—9.6
	Few	5	14	0.1
	Fair number	1	4	28.7
	Large number	8	23	72.9
	Total	16	45	
Fed with 76 to 228 milligrams nitrogen as calcium and potassium nitrates in addition to that in seed	None	..	..	..
	Few	6	18	—5.6
	Fair number	3	11	26.4
	Large number	8	26	74.5
	Total	17	55	

Table 4 summarises the results with peas. The experiments are arranged in accordance with the number of root tubercles observed at the time of harvest.

TABLE 5.

Experiments with Peas and Alfalfa, 1888–1889.

CONDENSED SUMMARY OF RESULTS AND AVERAGES.

	Root Tubercles.	Without Nitrogen in Nutritive Solutions.			With Nitrogen in Nutritive Solutions.			Total.		
		No. of Experiments.	No. of Plants in Experiments.	Average Gain (or Loss —) of Nitrogen.	No. of Experiments.	No. of Plants in Experiments.	Average Gain (or Loss —) of Nitrogen.	No. of Experiments.	No. of Plants in Experiments.	Average Gain (or Loss —) of Nitrogen.
				Mg.			Mg.			Mg.
Peas.	None	10	23	—9.6	6	13	—22.7	16	36	—14.5
	Few	7	21	—2.1	12	39	0.6	19	60	— 0.4
	Fair number	4	15	63.3	7	24	28.4	11	39	41.1
	Large number	10	30	77.9	18	69	99.5	28	99	91.7
Alfalfa.	None	..	..	..	..	..	..	..	..	..
	Few	..	..	..	3	4	84.0	3	4	84.0
	Fair number	1	3	137.5	..	..	..	1	3	137.5
	Large number	..	..	..	1	1	382.2	1	1	382.2

In Table 5 a condensed summary of Tables 3 and 4 is given. The results with Champion of England and East Hartford Early peas are arranged together.

(To be continued.)

THE INTERACTION OF SULPHURETTED HYDROGEN AND THE ORTHOARSENIATES OF THE ALKALI METALS.

BY LEROY W. MCCAY.

Berzelius, to whom we are indebted for the greater part of our information in regard to the sulphur compounds of arsenic, gives two methods for the preparation of the pentasulphide:

1. Saturation of a moderately concentrated solution of arsenic acid with sulphuretted hydrogen; 2. Decomposition in a strong solution, by means of sulphuretted hydrogen, of an alkali arseniate, and precipitation, by the addition of a mineral acid, of the penta-sulphide formed.

The action of sulphuretted hydrogen upon arsenic acid I have examined with much care, and, in the preparation of potassium sulphoxyarseniate through the action of the gas upon mono-hydrogen potassium arseniate, have obtained results which are in direct opposition to what the statements of Berzelius had led me to expect. It therefore seemed advisable to continue the work and to study the action of sulphuretted hydrogen upon the mono-, di- and tri-alkali arseniates. The results thus obtained prove beyond a doubt that although Berzelius' second method of preparation is in principle correct, yet it is successful only under definite conditions.

The reactions which take place in all three cases are almost identical with those which are characteristic of the action of sulphuretted hydrogen on arsenic acid alone or on alkali arseniates acidified with a mineral acid. The experiments may be classified as follows:

A.—*The Action of Sulphuretted Hydrogen on a Solution of Dihydrogen Potassium Arseniate.*

1. Sulphuretted hydrogen was passed in a rapid current for eight hours through a saturated solution of the salt. The precipitate formed was found to consist of mono-hydrogen potassium sulphoxyarseniate in beautiful crystals, arsenic pentasulphide, arsenic trisulphide and sulphur. The solution, after the removal of the precipitate by filtration, was soon again clouded, and in the fresh precipitate, along with mono-hydrogen potassium sulphoxy-arseniate, could be readily detected potassium arseniate and arsenite, and free sulphur. Pure arsenic pentasulphide cannot then be prepared by saturating in the ordinary way with sulphuretted hydrogen a *very concentrated* solution of dihydrogen potassium arseniate, and decomposing, through the addition of a mineral acid, the sulpho-salt formed.

2. The foregoing experiment was repeated with a moderately concentrated solution of dihydrogen potassium arseniate, but, with the exception of the failure of the sulphoxy-salt to crystallise out, the result was the same.

3. (*a*). 0.9 gram dihydrogen potassium arseniate was dissolved in water and the solution treated in the cold for fifteen hours with sulphuretted hydrogen in a rapid current. The gas, as far as was possible, was kept in large excess all the time. The solution became very yellow and some sulphide separated out, but the greater part of the arsenic remained in combination as a dihydrogen potassium sulpharseniate (?) in a state of semi-solution. A large excess of hydrochloric acid caused the solution to clear rapidly and the arsenic pentasulphide to be precipitated in a flocculent, sulphhydrated form. It was filtered out, washed according to Bunsen's directions (with alcohol and bisulphide of carbon), and weighed in a Gooch crucible, after having been dried at a temperature of 110° C.

Weight of Sulphide found.	Calculated.
0.7661 gram.	0.775 gram.

The filtrate contained sulphoxyarsenic acid, and the precipitate upon examination gave reactions for arsenic trisulphide.

(*b*). 0.9 gram of dihydrogen potassium arseniate was dissolved in water and treated with sulphuretted hydrogen, as above described, for twenty hours. The flask containing the solution was provided with a Bunsen valve to keep out the air, but the weight of the sulphide obtained was nevertheless low—0.768 gram. The filtrate contained no sulphoxyarsenic acid, but the precipitate was mixed with a little trisulphide.

(*c*). 0.9 gram of the salt was dissolved and treated with sulphuretted hydrogen for twenty hours, all air being carefully excluded by having the escaping gas bubble through water contained in a Volhard-Fresenius absorption apparatus which was attached to the flask containing the solution of the arseniate. The filtrate from the precipitated sulphide was free from sulphoxyarsenic acid, but the alcohol and bisulphide of carbon washings gave upon evaporation a notable amount of sulphur, and the precipitate itself contained arsenic trisulphide.

(*d*). 0.9 gram of the salt was put in a two-liter flask, dissolved in water and the solution diluted to about 1900 cm^3.; the solution was treated with sulphuretted hydrogen in a rapid current until an opalescence appeared. The flask was then filled almost full of cold freshly-boiled water, tightly corked and put away in a cold place for two weeks. Even in this case the formation of the

sulpho-salt was incomplete;[1] only 0.7665 gram of pentasulphide was obtained.

These experiments show that it is impossible to prepare pure arsenic pentasulphide, even from an *ordinary* solution of dihydrogen potassium arseniate, simply by treating the liquid for a long time in the cold with sulphuretted hydrogen in a rapid current.

4. (*a*). 0.9 gram salt was dissolved in water, the solution diluted to about 500 cm^3., heated in a flask to boiling, and treated for eight hours with sulphuretted hydrogen in a rapid current. The heating was then discontinued, but the gas was permitted to flow until the solution had become cold; the flask was then tightly corked and set aside for a day and a night. The pentasulphide thus formed amounted to 0.7758 gram, the theoretical quantity being 0.7750 gram. The washing was very thorough, large quantities of alcohol and bisulphide of carbon being used. By properly diluting, then, the solution of the dihydrogen potassium arseniate and keeping it *hot*, it is possible by Berzelius' second method to prepare pure arsenic pentasulphide. The following mode of procedure proved all that could be desired:

(*b*). 0.9 gram dihydrogen potassium arseniate was dissolved in water and the solution brought into a bottle, in which it was saturated with sulphuretted hydrogen, and heated under pressure in a manner which I have before described. The solution, at the end of the time, had the same peculiar appearance exhibited by that in experiment 3; the sulphide refused to settle. The addition of strong hydrochloric acid, however, brought about the complete separation of the sulphide, in amount 0.7750 gram; or, calculating as arsenic, 0.3750 gram. These figures coincide with the calculated weights of arsenic pentasulphide and arsenic. The sulphide was evidently pure.

[1] The result of this experiment was so unlooked for that I repeated it, strongly acidifying the solution with hydrochloric acid, however, before saturating with sulphuretted hydrogen, and obtained at the end of the two weeks 0.7746 gram of arsenic pentasulphide instead of the calculated 0.775 gram. In the case of arsenic acid, then, the passage *in the cold* from the oxy-salt through the sulphoxy-salt to the sulpho-salt takes place slowly, but smoothly and completely, whereas in the case of the corresponding acid salt, when the sulphoxy stage is reached, there is a partial decomposition into alkali arsenite and sulphur, and that, too, in spite of the presence of an excess of sulphuretted hydrogen.

As will be seen further on, this extraordinary deportment while in the sulphoxy state is not shown by the two other ortho-salts.

B.—*The Action of Sulphuretted Hydrogen on Hydrogen Dipotassium Arseniate.*

5. To a solution of arsenic acid potassium hydrate[1] was added until the solution possessed a slightly alkaline reaction. Sulphuretted hydrogen was then passed into the liquid until it seemed saturated. After standing twelve hours the solution was decomposed with an excess of sulphuric acid. The precipitate proved to be a mixture of arsenic trisulphide and pentasulphide with sulphur, while the filtrate evidently contained sulphoxyarsenic acid, arsenic acid and arsenious acid. The large amount of arsenic pentasulphide found was evidence of the formation of considerable sulpharseniate.

6. 100 cm^3. of a solution containing 20 grams of pure arsenic acid in 2000 cm^3. of water were diluted, rendered faintly alkaline with potassium hydrate, treated for six hours with sulphuretted hydrogen in a rapid stream, and finally decomposed with an excess of hydrochloric acid. The precipitate was washed according to Bunsen's directions, dried at 110° C., and weighed in a Gooch crucible. The sulphide weighed 1.0758 gram, while the theory calls for 1.0913 gram. The filtrate contained small quantities of sulphoxyarsenic acid, which fact explains the low result.

7. 100 cm^3. of the above solution were diluted, made faintly alkaline with potassium hydrate, treated for eighteen hours with sulphuretted hydrogen in a rapid current, and then decomposed with an excess of hydrochloric acid. The precipitate, after proper treatment, weighed 1.0892 gram; calculated weight, 1.0913 gram. The precipitate was therefore practically pure arsenic pentasulphide. The filtrate gave no reactions for sulphoxyarsenic acid.

8. 100 cm^3. of the standard solution, after having been diluted, treated with potassium hydrate until faintly alkaline, heated in a flask upon the water-bath, and treated for three hours with sulphuretted hydrogen, contained all the arsenic in the form of sulpho-salt. The sulphide weighed 1.0913 gram; calculated weight, 1.0913 gram.

9. 100 cm^3. of the arsenic acid solution were made faintly alkaline, diluted, saturated with sulphuretted hydrogen, and for one hour heated under pressure in a bottle. Weight of sulphide

[1] I used potassium hydrate, but sodium hydrate or ammonium hydrate will serve the same purpose.

found, 1.0938 gram; calculated weight, 1.0913 gram. This precipitate was also pure pentasulphide. The filtrate was free from sulphoxyarsenic acid.

C.—*The Action of Sulphuretted Hydrogen on Tripotassium Arseniate.*

10. A solution of arsenic acid made strongly alkaline, and treated with sulphuretted hydrogen for a few hours in the cold, showed all the reactions which were noticed in Exp. 6, with the exception that no sulphur separated.

11. 100 cm^3. of the standard solution were made strongly alkaline with potassium hydrate, and treated with sulphuretted hydrogen for about eighteen hours. The sulpho-salt alone was formed, and, when decomposed by means of an excess of hydrochloric acid, yielded 1.0925 gram arsenic pentasulphide.

12. 100 cm^3. of the standard solution, having been made strongly alkaline, were heated on the water-bath for four or five hours and treated continuously with sulphuretted hydrogen in a rapid current. On addition of hydrochloric acid a precipitate was formed, which, after thorough washing with alcohol and bisulphide of carbon, weighed exactly 1.0913 gram. This is just what the theory demands.

13. 100 cm^3. of the arsenic acid solution, having been rendered strongly alkaline by addition of potassium hydrate, treated with excess of sulphuretted hydrogen and heated in a bottle in the water-bath for one hour, gave, after the sulpho-salt had been decomposed with hydrochloric acid, a precipitate which weighed 1.0925 gram. Here also the reaction was complete, all the tripotassium arseniate having been transformed into the corresponding sulpho-salt.

It is therefore true that arsenic pentasulphide can be prepared by saturating an alkali-metal orthoarseniate with sulphuretted hydrogen and decomposing with excess of a mineral acid the sulpho-salt formed, but this process is only complete provided: (1) the solution of the arseniate is properly diluted and kept hot, and the sulphuretted hydrogen passed in excess and for a long time (dihydrogen salt), or, (2) the sulphuretted hydrogen is kept present in such large excess and passed for such length of time that there is no chance for the potassium sulphoxyarseniate (which is always formed in passing in the wet way from

arsenic acid to sulpharsenic acid) to split up into potassium arsenite and sulphur, or to escape subsequent complete transformation into the sulpho-salt (di- and tri-alkali salts). This method is admirably adapted for preparing large quantities of arsenic pentasulphide, and that it can be used for the determination of arsenic with a satisfactory degree of accuracy is evident from the results of the quantitative determinations above described.

The results described in this paper will, I think, serve to clear up much of the mystery connected with the subject of the formation of the alkali sulpharseniates in the wet way. The existence, unstable character, and mode of decomposition of sulphoxyarsenic acid and its salts appear fully capable of accounting for the hitherto seemingly abnormal interaction of sulphuretted hydrogen and the orthoarseniates of the alkali metals.

In conclusion I should say that a number of experiments which I have recently made, have led me seriously to question the accuracy of the views of Berzelius regarding the action of the alkali hydrates on the sulphides of arsenic. I hope before long to be able to speak more definitely of the subject. In the meantime I reserve for myself the right further to investigate the matter.

PRINCETON, N. J., *July* 1, 1890.

THE INDIAN GRASS OILS.

BY F. D. DODGE.

The preparation and properties of citronellic aldehyde, $C_{10}H_{18}O$, the principal constituent of oil of citronella, have been described in a previous paper.[1] A sample of the aldehyde was prepared from thoroughly washed bisulphite compound and redistilled twice. It is a colorless oil, apparently unaltered by light or long standing in a closed vessel, but readily oxidising on exposure to the air.

Its density at 20° is 0.8560.

The observed rotation of the pure substance in a 4-dm. tube, Laurent polarimeter, was $+16° 34'$ (mean of 10 observations), whence: $[\alpha]_D = +4° 50'$.

[1] This Journal **12**, 7.

The index of refraction was determined in the spectroscope, with glass prism of 59° 42′, at 20° C.

Index (n) for $H\alpha = 1.442$ for Li line $= 1.4415$
$H\beta = 1.4515$
$H\gamma = 1.4577$ " Na " $= 1.4448$;

whence specific refraction $\frac{n^2-1}{(n^2+2)d} = 0.3091$, and molecular refraction $R\alpha = 47.60$.

The calculated refractions are:

1. For the "open-chain" formula, $C_4H_9-CH=CH-C_3H_6-COH$, or a similar one:

C_{10}	$= 24.80$
H_{18}	$= 18.72$
O in $>C=O$	$= 2.34$
Increment for $-CH=CH-$	$= 1.78$
	47.64

2. For an aldehyde having a hexatomic nucleus like the menthol series:

C_{10}	$= 24.80$
H_{18}	$= 18.72$
O in $>C=O$	$= 2.34$
	45.86

There can be little doubt, therefore, that citronellic aldehyde is an open-chain compound and is homologous with acrolein and the aldehydes of the $C_nH_{2n-2}O$ series.

Cymene from Citronellic Aldehyde.

The bromine addition-product of citronellic aldehyde decomposes on heating, as already shown, yielding an oil having the properties of ordinary cymene. From 100 grams of aldehyde, 13 grams of cymene, boiling at 175°–180°, were obtained. Oxidation with dilute nitric acid afforded a crystalline acid, melting at 177°, which was undoubtedly impure para-toluic acid. By treating citronellic aldehyde with iodine and distilling the product, no cymene was obtained, but a hydrocarbon, boiling near 160°, which has not yet been identified.

Citronellal-phosphoric Acid.

The occurrence of a crystalline compound among the products of the action of phosphoric anhydride on citronellic aldehyde has already been mentioned. The conditions under which this substance was formed were then unknown and several efforts to obtain sufficient for analysis were unsuccessful. Some months later I obtained, from an experiment in which the phosphoric anhydride was added to a cooled solution of the aldehyde in an equal volume of *moist* ether, about two grams of pure substance, which crystallised from alcohol in large transparent prisms and square plates.

This compound is a strong acid, decomposing and dissolving in alkaline carbonates and being reprecipitated on addition of mineral acids.

Analyses gave the following results:

I. Substance, 0.2138 gram; CO_2, 0.4009 gram; H_2O, 0.15695 gram.

II. Substance, 0.1893 gram; $Mg_2P_2O_7$, 0.0943 gram.

III. Substance, 0.2163 gram; $Mg_2P_2O_7$, 0.1034 gram.

	Calculated $C_{10}H_{19}PO_4$.	I.	II.	III.
C	51.28	51.13	...	...
H	8.11	8.11	...	...
P	13.25	...	13.9	13.34

Titration with standard alkali showed that the compound is a monobasic acid, its acid properties being undoubtedly due to a phosphoric group, for the oxidation of the aldehyde group seemed, under the conditions of formation, very improbable. This being the case, the reaction producing the compound is not simply a dehydration, but requires the presence of one or more molecules of water. In fact, in all cases in which any of this acid has been obtained water has been present, the ether used being nearly saturated; while, if all moisture is carefully excluded and the reaction carried on in a dry benzene solution, no product is obtained.

Although the most favorable conditions for the preparation of this substance have not yet been determined, I have obtained moderate quantities by the following process:

5 grams phosphoric anhydride are covered with 20 cc. dry benzene; the necessary amount of water (1 molecule) is now added,

dissolved in ether, *i. e.* 31 cc. saturated ether. The vessel is kept as cool as possible. A cake of metaphosphoric acid forms and the greater part of the liquid is then poured off, 10 grams aldehyde (or, equally well, 20 grams citronella oil) slowly added and the whole well mixed. The vessel is allowed to stand at 70° several hours. Concentrated sodium carbonate is then added until the solution is alkaline, the excess of oil separated, and the aqueous solution (kept as concentrated as possible) is extracted with ether until colorless. If it is still colored a few drops of hydrochloric acid are added and the solution again extracted, this cautious acidifying being repeated till the liquid, after extraction, is perfectly colorless. An acid by-product seems to be formed in the reaction, which is precipitated by hydrochloric acid before the phosphoric derivative. Excess of concentrated hydrochloric acid is now added, the solution chilled and filtered, and the precipitated acid crystallised from warm dilute alcohol.

The alcoholic solution should be colorless; if much oil is present it can be removed by fractional precipitation with water or by washing the crystals of the acid with dry ether. The yield of acid is about two grams.

The solution from which the acid has been thrown down by hydrochloric acid will generally afford more product on concentration. Much of it, however, is decomposed by the continued action of the hot water, with formation of an oil. In some cases I have noticed the separation of long needles from this solution. These melt at 180° and are readily volatile; their nature is not yet ascertained. Ordinary glacial phosphoric acid does not answer for the preparation of this compound; I have obtained it only by the use of phosphoric anhydride and water.

Properties.—It is sparingly soluble in water, readily in alcohol, with difficulty in ether. Its crystalline form varies: from alcohol, or ether-alcohol, and generally by slow crystallisation, it forms square plates; from dilute alcohol, and sometimes from water, prisms or long flat needles are obtained. Its system is not yet determined. It melts near 203°. It is moderately stable in the presence of aqueous acids, but warm alkalies decompose it with formation of oil. As already shown it is a monobasic acid. The potassium salt is very soluble and crystallises in long needles; the sodium salt crystallises more readily and in forms resembling those of the free acid. The ammonium salt resembles the potassium salt.

Aniline citronellal-phosphate is readily obtained by adding aniline in slight excess to an alcoholic solution of the acid. Ether precipitates the salt in white needles melting at 165°. The quinoline salt also crystallises in needles. As was to be expected, citronellal-phosphoric acid is optically active. A solution of 5.84 grams in 100 cc. of 95 per cent. alcohol showed a rotation in a 2-dm. tube of $+2°\ 58'$. I have not succeeded in determining whether the crystallised acid is also active. As is well known, there are but few substances which are rotatory both in solution and in the crystalline form.

Constitution.—The most obvious formula for citronellal-phosphoric acid is

$$C_9H_{17}-CH<\begin{matrix}O\\O\end{matrix}>PO-OH,$$

which expresses the fact, among others, that in the aldehyde the group —COH alone takes part in the reaction. Evidence on this point is afforded by the fact that the solution of the sodium salt of the acid does not reduce ammoniacal silver solution even on boiling. If this supposition be true, there is no apparent reason why other aldehydes should not react similarly. In the literature of aldehydes, however, no mention is found of such phosphoric derivatives. An analogous body may be the crystalline compound of cinnamic aldehyde with nitric acid, discovered by Dumas and Peligot.[1] I have made a series of experiments in the endeavor to prepare phosphoric derivatives of other aldehydes, as yet unsuccessfully. No such compound could be obtained from cinnamic aldehyde, benzaldehyde, chloral, œnanthol, or citriodoric aldehyde (the constituent of lemon grass oil below described). This work, however, is not yet finished.

The action of heat on citronellal-phosphoric acid and its salts, and its oxidation and reduction products, will be reserved for a subsequent paper.

Lemon Grass Oil.

The uncertain botanical origin of this oil, its similarity in properties to citronella oil, and the fact that its principal constituent is a peculiar aldehyde, have been noted in the first paper (l. c.). With the assistance of Mr. Geo. A. Ferguson, a student in this laboratory, I have been enabled to investigate the oil more closely. The sample used was a Ceylon oil, redistilled in this city. It has a light yellow color and possesses the very characteristic odor of

[1] Ann. Chem. (Liebig) **100**, 104.

the lemon verbena. The specific gravity at 22° is 0.886; at 15.5°, 0.8955.

On distillation the oil boils between 200° and 240,° a small residue being not volatile at the latter temperature. The principal fraction was from 220°–225°. The oil appears to suffer less alteration or to be more homogeneous than citronella oil, which may be due to its recent redistillation. No indications of the presence of mineral oil or paraffins were observed. The reactions of the oil with ammoniacal silver solution, with phenylhydrazine, and with acetyl chloride, are the same as with citronella oil. With sodium bisulphite, however, its behavior is quite different, and, as far as I am aware, unique.

Isolation of the Aldehyde.

In the earlier experiments we proceeded exactly as with citronella oil. 150 grams bisulphite, in saturated solution, were added to 200 cc. oil. A white magma was obtained, which was pressed and washed with ether. The dry precipitate was mixed with crystallised sodium carbonate and the aldehyde distilled off in a current of steam. When an excess of oil is used the reaction proceeds as in the case of citronella, but when the amount of bisulphite is increased a different result is obtained and the isolation of the aldehyde becomes simplified. The following process we have found most convenient: 1000 grams dry bisulphite are dissolved in 5 liters hot water; while still slightly warm, 1 liter oil is added at once. The mixture is vigorously stirred for several minutes; it soon becomes very warm, and a pasty mass of bisulphite compound results. After two or three hours, however, the precipitate will have entirely redissolved, leaving a heavy solution, containing the aldehyde, and a layer of residual oil (300 cc.) above. In 24 hours the solution is perfectly clear and may be siphoned off and filtered.

Concentrated sodium hydrate is added to the filtered solution until strongly alkaline, and, after 24 hours, the supernatant layer of liberated aldehyde is separated, filtered and dried.

The product is a yellow oil of very pleasant citrine odor. The yield reaches 65–68 per cent. of oil employed. Redistillation with steam lightens the color; it distills very slowly and we have not yet obtained it colorless. We were unable to detect any difference in properties between this oil and that obtained from the solid bisulphite compound.

The aqueous liquid containing the aldehyde has curious properties. It may be concentrated at 100° without apparent alteration, becoming more and more viscid until its density reaches 1.4, when on cooling it becomes supersaturated, and slight agitation, rubbing with a glass rod, etc., will cause immediate solidification. By cautious evaporation we have, in one case, obtained transparent crystals an inch in length, whose analysis will be given later. It is evident that in this solution we are not dealing with a typical bisulphite solution, as in the case of vanillin, or phenanthrenequinone, for the aldehyde is not set free by acids. On adding to this liquid an equal volume of concentrated hydrochloric acid the result is a thick precipitate of salt, while the aldehyde remains in solution. Barium chloride produces an abundant precipitate of sulphite and sulphate. By removing excess of barium with sodium carbonate and filtering, a liquid is obtained, which may be concentrated as before and still contains the aldehyde. If a little sulphuric acid is added it can no longer be concentrated, but darkens on heating and liberates sulphurous acid. Caustic alkalies, however, instantly set free the aldehyde. If this liquid were merely a solution of a typical bisulphite compound in excess of bisulphite, further addition of aldehyde should cause the whole to precipitate. This does not occur; the solution seems to be without effect on the aldehyde.

All the observed facts indicate the presence of a curious combination of aldehyde, sulphurous acid and soda—most probably a complex one, for the concentrated solution diffuses very slowly, behaving in fact somewhat like a gelatine solution.

The analysis of the above-mentioned crystals also points to a complicated formula:

5.0026 grams lost at 100° 2.650 grams H_2O, or 52.9 per cent.

Na in dry salt = 27.6 per cent.
S " " " = 22.48

The tentative formula $C_{15}H_{16}O_2.2NaHSO_3.4Na_2SO_3.50H_2O$ requires—

H_2O	52.	per cent.
Na in dry substance	27.1	
S " "	22.6	

The analyses will be repeated on fresh material. On heating these crystals they readily fuse in the crystal water—the latter is almost entirely lost by standing over sulphuric acid. Further

heating liberates the organic portion in fumes which resemble the aldehyde in odor, and the residue appears to be entirely sodium sulphite.

Properties.—This substance is a light yellow liquid, with an odor like that of the original oil, but less penetrating. Its density at 15.5° is 0.8968. It begins to boil near 225°, with gradual decomposition or alteration. Analysis:

	Calculated for $C_{10}H_{18}O$.	Found.
C	78.94	78.79
H	10.52	10.82

The aldehyde is then isomeric with camphor, and, from its most evident property, we propose for it the name *citriodoric aldehyde.* Vapor density determinations have not as yet given concordant results. In a 1-dm. tube a rotation of + 1°30′ was observed, but the sample was not colorless and the result is uncertain. Consideration of the possible formulæ of this substance indicates that it is probably inactive.

Owing to the instability of the bromine addition product we were unable to determine the unsaturation by titration. Determination of the molecular refraction has not given a satisfactory result, owing to the lack of a perfectly pure specimen; the dispersion is much greater than in the case of citronellic aldehyde.

With silver solution, phenylhydrazine, aniline, and paratoluidine, the behavior of the aldehyde is like that of citronellic aldehyde.

Action of Dehydrating Agents.

Citriodoric aldehyde, being isomeric with camphor, should yield on dehydration para-cymene or one of its isomers. Such, under certain conditions, is the case. By the action of phosphoric anhydride on the aldehyde dissolved in 10 parts of ether, the temperature being kept low, no cymene or light oil is obtained, but there results an oil of offensive odor, boiling at 200°–260°, and a fluorescent substance not volatile at 260°. Semmler[1] also noticed among the products of the action of phosphoric anhydride on geraniol a poly-terpene which showed beautiful dichroism. By direct action of phosphoric anhydride (50 grams) on the aldehyde (25 grams), a distillate of 6 grams was obtained, passing over between 170° and 200°. This possessed the odor of cymene, and was identified as *para*-methyl-propyl-benzene by oxidation

[1]Ber. d. chem. Ges. 23, 1098.

with excess of hot permanganate and conversion of the resulting insoluble acid into the characteristic crystals of methyl terephthalate, melting at 140°.

Zinc chloride does not appear to produce cymene. Concentrated hydrochloric acid acts very readily on the aldehyde, with evolution of heat. The product is a dark red oil, from which, by distillation with steam, cymene is readily separated, the yield reaching 50 per cent. The residue is a dark viscid product of peculiar odor. The cymene is the ordinary modification, as was shown by conversion into para-toluic acid, melting at 180°. This simple transformation of a probably "open-chain" compound into an aromatic hydrocarbon is remarkable.

Reactions.—By treatment with zinc dust in acetic acid solution a product was obtained which probably contains the corresponding alcohol. It has a peculiar odor, is decomposed on distillation, and has not yet been purified.

Oxidation by dilute permanganate affords a mixture of acids. Neither acetic nor valeric acid was detected.

Alcoholic ammonia reacts with the aldehyde at 150°–170°, with formation of an unstable product, not yet identified.

The oxime was obtained as an aromatic oil which could not be induced to crystallise.

Constitution.—As yet we have few facts on which to construct a formula for this compound. The formation of para-cymene by simple condensation establishes, as in the case of citronellic aldehyde, the presence and position of a methyl and a propyl group. It seems probable also that the aldehyde is a fatty derivative with two ethylenic bonds. Whether it is the aldehyde corresponding to geraniol (see below) or not, it is impossible as yet to say.

Residual Oil.

The portion of lemon grass oil, which does not combine with bisulphite, was fractioned. We obtained indications of the presence of a terpene, but the oil alters very rapidly on distillation. It seems probable also that cymene is present in the oil, as it would easily result from condensation of the aldehyde.

Indian Geranium Oil.

The oil obtained from *Andropogon schoenanthus* L. has been known as: Rusa, Row-sah, Rosa, Rosé, or Roisa oil; oil of

Namur, Nimar, Namar or Namaur; Khandesh oil, Palmarosa oil; ginger-grass, Indian or Turkish geranium oil; Ingweröl; and also by many native names. Oils of ginger-grass and Turkish geranium are distinct commercially and have different market values. There is little doubt, however, that they represent different qualities of the same oil.

Stenhouse[1] and Gladstone[2] examined oils supposed to be the one in question, but the first insight into the nature of the geranium oil is due to Jacobsen,[3] who found the principal constituent to be a substance boiling at 232–3°, to which he assigned the name *geraniol.*

Geraniol has the composition $C_{10}H_{18}O$ and is isomeric with borneol, cineol, and menthone. It is a colorless, strongly refractive liquid, of peculiar, rose-like odor; it is miscible with alcohol and ether, and insoluble in water; it does not solidify at —15°; its boiling point is higher than that of any of its isomers, and it is optically inactive. On exposure to the air it is very gradually altered, absorbing oxygen and becoming a thick, viscid mass. The density of geraniol at 15° was 0.8851; at 21°, 0.8813. Fusion with potash, digestion with barium hydrate, or oxidation with permanganate yields iso-valeric acid. Distillation with phosphoric anhydride or zinc chloride produces a terpene, *geraniene*, $C_{10}H_{16}$.

Geraniol readily absorbs hydrochloric acid gas, with formation of a compound analogous to bornyl chloride. In fact it resembles borneol in most of its reactions and is probably a monatomic alcohol. The physical difference, that it is liquid and inactive, is true of nearly all its derivatives. Geranyl chloride, $C_{10}H_{17}Cl$, is a yellow oil, of peculiar aromatic odor. It does not solidify at —15°, and decomposes on heating. Various ethers of geraniol have been prepared from the chloride by reaction with potassium salts. Geraniene, $C_{10}H_{16}$, boils at 162°–164°, and is inactive; it forms a liquid hydrochloride, but no hydrate, when treated by Wiggers' method.

I have examined several samples supposed to be Indian geranium oil. One specimen was found to behave exactly as Stenhouse has described. About one-half of the oil distilled below 180°, leaving a viscid residue. No portion corresponding to geraniol was obtained. The distillate consists probably of a

[1] J. Chem. Soc. 1844, 122. [2] Ibid. 1864, 10.
[3] Ann. Chem. (Liebig) **157**, 232.

terpene or terpenes. Not being confident that this was genuine oil I made no further examination of it.

A sample of ginger-grass oil from Ceylon gave better results; it seemed to be the oil described by Jacobsen. On distillation it passed over between 150° and 260°, leaving considerable residue. The portion between 100° and 170° contained water and ordinary alcohol. The principal fraction was 227°–233°; which possessed the properties ascribed to geraniol.

This product shows great similarity to the substance isolated from citronella oil and termed provisionally "citronellyl alcohol." The latter, however, boiled some 10° lower, which might be due to admixed terpene, and further purification was desirable.

Haller[1] has shown that camphor and borneol may be separated by treatment with a dibasic acid. Borneol, being an alcohol, forms an acid ether which is soluble in alkalies. It seemed probable that this process could be applied for the purification of the desired alcohol.

16 grams of "citronellyl alcohol," boiling at 222°, were heated with 13 grams of succinic acid in a tube, at 140° to 180°, for fifty hours. The contents of the tube were washed with ether, the ether solution extracted with potassium carbonate solution, and the latter, again, extracted with ether to remove traces of oil. The alkaline solution was then heated with dilute caustic potash and the liberated oil collected and fractioned. It was found to boil at 225°–230° and possessed a faint odor of roses.

Analysis gave an unsatisfactory result:

	Calculated.		Found.
	$C_{10}H_{20}O$.	$C_{10}H_{18}O$.	
C	76.92	77.92	75.96
H	12.82	11.70	12.79

Geraniol, treated in this way, gave a very similar product, which was unfortunately lost before an analysis was made.

My work had reached this point when an investigation of Indian geranium oil, by F. W. Semmler, was published.[2] He has confirmed Jacobsen's results and has shown that geraniol has the composition $C_{10}H_{18}O$, and that the molecular refraction indicates the presence of *two* "ethylenic" bonds. Hence a ring structure is inadmissible (as in the case of citronellic aldehyde), and geraniol must be classified with the "open-chain" unsaturated alcohols, $C_nH_{2n-2}O$.

[1] Compt. rend. **108**, 1308. [2] Ber. d. chem. Ges. **33**, 1098.

Cautious oxidation of geraniol by permanganate yields valeric acid in nearly molecular quantity.

From these facts he deduces as the most probable structure of geraniol:

$(CH_3)_2 - CH - CH_2 - CH = CH - C(CH_3) = CH - CH_2OH,$

according to which it should be inactive, and very closely related to the active citronellic aldehyde, whose provisional formula has been given as:

$(CH_3)_2 - CH - CH_2 - CH = CH - CH(CH_3) - CH_2 - CH = O.$

As Herr Semmler has expressed his intention of continuing his work, I have given up further experiments on this oil. When in possession of more material, however, I hope to solve the question of the identity of geraniol with "citronellyl alcohol."

In reviewing the results thus far obtained in the study of the grass oils a few general facts become apparent. The constituents of the oils belong to the unstudied group of compounds which have an open-chain structure and readily suffer condensation, yielding terpenes, para-cymene, or derivatives of the latter.

This group is quite probably a large one, but as yet citronellic and citriodoric aldehydes and geraniol are the only members whose structure is even approximately known. The alcohol, $C_{10}H_{18}O$, and aldehyde, $C_{10}H_{16}O$, found by Bruylants[1] in oil of tansy, doubtless fall also in this group.

Isomeric with geraniol and citronellic aldehyde are borneol, cineol, terpineol and menthone, all of which have a six-atom nucleus, while of the ten or more substances having the composition $C_{10}H_{16}O$, camphor is the only one whose structure is known, this also having a six-carbon ring.

It is remarkable that the two aldehydes found in citronella and lemon-grass oils differ from all known aldehydes in two peculiar properties; the first, in forming citronellal-phosphoric acid, the second, in yielding the stable bisulphite solution.

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[1] Ber. d. chem. Ges. **11**, 449.

THE CO-EFFICIENT OF MINERAL CONDENSATION IN CHEMISTRY.

By T. Sterry Hunt.

§1. That the solid and liquid mineral species known to us (including under the designation of minerals all distinct forms of unorganized matter) are formed by a process of intrinsic condensation or so-called polymerisation from simpler chemical species, which are themselves often gaseous, and, moreover, that this condensation is very considerable, is a conclusion to which chemists have been naturally led. The problem of fixing its amount, or, in other words, of determining the co-efficient of the condensation which results in the production of such mineral species, is one which must present itself to every earnest student of chemical physics, but has nevertheless hitherto been generally disregarded. A reason for this neglect of the problem is to be found in the belief that it does not admit of solution, as may be shown by citations from the writings of many eminent chemists.

§2. Thus Wolcott Gibbs in 1877, after reviewing the researches of his predecessors, Marignac, Scheibler, H. Deville and Debray, on the various polytungstates and polymolybdates, and his own important contributions to the subject, describes these various bodies as salts of "complex inorganic acids," and proceeds to illustrate by formulas the results of their chemical analysis. Of a certain hydrated phosphovanadotungstate of barium examined by him he declares that "it has the highest molecular weight yet observed, 20,058." By this we are to understand no more than that this number corresponds to the simplest chemical formula admissible, for he further says, "We have no positive knowledge of the composition of these salts, their molecular weights being, as in the case of most inorganic compounds, entirely unknown," adding that research "tends constantly to show that the structure of inorganic bodies is more complex than was formerly supposed."[1] The language of Roscoe in 1884 embodies the same thought when he speaks of looking forward to "the establishment of a systematic inorganic chemistry which need not fear comparison with the organic branch of our science"; and adds, referring to the complex inorganic acids of Gibbs: "It is well to be reminded that

[1] Gibbs: Complex Inorganic Acids, Am. J. Sci. (3) **14**, 61.

complexity of constitution is not the sole prerogative of the carbon-compounds, and that before this systematisation of inorganic chemistry can be effected we shall have to come to terms with many compounds concerning whose composition we are as yet wholly in ignorance."[1] It may be remarked, in passing, that the retention by these writers of the old antithesis between organic and inorganic chemistry, as distinguishing carbonaceous compounds from other species, can only serve to hinder the systematisation and the unification of the facts of the science.

Still more recently, in 1889, Victor Meyer, in his address before the Association of German Naturalists and Physicians at Heidelberg on The Chemical Problems of To-day, says with regard to the question of intrinsic condensation: "We know to-day very well that the silicon oxide cannot have the formula SiO_2, and that this must be multiplied by a very large factor, but of the numerical value of this last we have no indication." Further he adds: "We lack the least knowledge in regard to the true molecular weight of minerals."[2]

§3. The direct and concise language of Louis Henry of Louvain, in 1879, may be taken as a fuller expression of the opinions generally entertained by chemists on this subject up to the present time. Having shown that for most oxides of the elements the normal forms corresponding with the chlorides, as in the case of iron, aluminum, titanium, silicon, etc., are unknown, and that we possess only greatly condensed polymers of these oxides $(RO_x)_n$, he proceeds to inquire: "What is the true value of n, the co-efficient of polymerisation, or, in other words, what is the real molecular formula of these polymeric oxides? These questions are doubtless of great interest, but it should be stated at once that it is absolutely impossible to give a direct answer. I do not know of any fact which would allow us to assign an absolute value to the co-efficient of polymerisation, n. . . . So far as facts will permit a conclusion, we may affirm that in most cases this number is very high, though different for different oxides."[3]

[1] Roscoe: Address to the Chemical Section of the Brit. Assoc. Adv. Science, at Montreal in 1884; Report, p. 663.

[2] Deutsche Rundschau, Nov. 1889; translated by L. H. Friedberg in the J. Am. Chem. Soc. **11**, 101.

[3] Louis Henry: Etudes de Chimie Moleculaire, Part I; Les Oxides Metalliques, Ann. Soc. Scient. Brux. 1879. A translation of this, by Prof. T. Carnelley, entitled "The Polymerisation of Metallic Oxides," appears in the L. E. and D. Philos., May and August, 1885. See farther the author's "New Basis for Chemistry," pp. 117–122; also ibid., 2d ed., p. 217, note.

§4. The same important questions had been propounded by the present writer in 1853, when, after noting that the equivalent weights for volatile bodies are known from the densities of their vapor, but in the case of non-volatile bodies are assumed, it was said that "having determined the true equivalent of a species from the density of its vapor, the inquiry arises whether a definite and constant relation may not be discovered between its vapor-density and the specific gravity of a species in its solid state. Such a relation being established, and the value of the condensation in passing from a gaseous to a solid state being known, the equivalents of solids, like those of vapors, might be determined from their specific gravities." The question was then asked, "What is the value of the condensation which takes place in the change from the gaseous to the solid state? or, in other words, what equivalent corresponds to a given specific gravity in any crystalline solid?" It was further said: "The equivalent of a crystallised species may often be a multiple of that deduced from those chemical changes which commence only with the destruction of its crystalline individuality." This point was then illustrated by examples in the history of various soluble crystalline species.[1]

§5. The question thus proposed by the writer in 1853, and repeated by Louis Henry in 1879, was persistently kept in view by the writer, and discussed at intervals in many published papers until 1886, when he arrived at what he has elsewhere put forth as, in his opinion, a simple and natural solution. This is found in the conclusion that the volume not only of gases and vapors but of all species, whether gaseous, liquid or solid, is constant, and that the integral weight—being the so-called equivalent or molecular weight—varies directly as the density, for which he proposes as the unit that of hydrogen at the standard temperature and pressure of 0° and 760 mm.

In all cases of polymerisation and depolymerisation of gases and vapor, or, in other words, of intrinsic condensation and intrinsic expansion at ordinary pressure, the law of volumes, so far as known, holds good; that is to say, these changes are subordinate to a simple ratio of volumes. This same law, it is here maintained, applies

[1] "The Theory of Chemical Changes and Equivalent Volumes," Am. J. Sci., March, 1853 (**15**, 226–234); also in L. E. and D. Philos. (4) **5**, 526; and in a German translation in the Chem. Centrbl. 1853 (p. 849). This paper is reprinted in the author's Chem. and Geol. Essays (1874), pp. 426–437. See also "A New Basis for Chemistry," Chap. IV.

equally to the production of dense vapors of liquids under increased pressure at temperatures above their critical points. Such dense vapors are polymers, which, on reduction of temperature, pass into liquid or solid polymers; the law of condensation by volumes being, by the present hypothesis, assumed to be a universal one. The relations here indicated have been elsewhere considered at length, when, after discussing the law of volumes in ordinary cases of condensation or polymerisation, it was said: "All analogy leads us to extend this law to the still greater condensations observed in the dense vapors into which liquid species above their critical points are resolvable, and to the farther condensation of these vapors into liquid and solid forms—to assume, in fact, that the law of combination by volume, like that of combination by weight (with which, so far as experience shows, it is indissolubly linked), is universal."[1] If this assumption, which appears to be in accordance with all the facts known, be admitted, the great problem proposed, namely, the fixing of the co-efficients of condensation for liquid and solid species, though a complex one, is solved.

§6. As a preliminary to a further treatment of this problem it here becomes important to note the relations between what (§1) we have designated respectively as the "chemical species" and the "mineral species." This will, moreover, serve to explain the language used in 1853, and cited above in speaking of crystalline species, as to "those chemical changes which commence only with the destruction of crystalline individuality." We may perhaps best approach the subject by conceiving the characters of a given species to be imposed upon matter by a force which is the form of that species, and which makes it what it is. The permanence of what we recognise as elementary species, in opposition to the notion of their transmutability, is the foundation of our chemical science, and from this it follows that secondary forms are imposed upon these, and present an ascending series; often passing through two or more chemical forms before receiving the mineral form, which may be in turn subordinated to some biotic form.

§7. These relations may be illustrated by well-known chemical facts: acetic and formic aldehydes and their sulphur and chlorine derivatives present many instructive cases of polymerism available

[1] See "A New Basis for Chemistry," in several chapters, and further in chap. XIV of the 2d ed. thereof. Also in an essay on "The Foundations of Chemistry," §15–19, This Jour. **10**, 344, from which the above extract is taken, and Chem. News **58**, 193, 205, 212.

for our purpose. Thus acetaldehyde, itself a very light and volatile liquid, is readily transformed into a denser and less volatile species, paraldehyde, which becomes a crystalline solid at 0°, melting at 10°, and having a vapor-density equal to $3(C_2H_4O)$, or three times that of the normal aldehyde, into which, however, it is easily changed. The same aldehyde also gives a less fusible crystalline polymer, metaldehyde, the integral weight of which, from the facility with which it reverts without melting to the normal vaporous aldehyde, is unknown. Again, formaldehyde is a gas soluble in water, from which by heat it is in part expelled and in part changed into a white volatile, crystalline solid insoluble in water, alcohol or ether, melting at 152°, but passing at a lower temperature into a gas having the density of the normal formaldehyde. A similar change is also effected when it is heated with water under pressure to a temperature above 100°, the normal aldehyde being taken into solution. This insoluble body, which is sometimes called methylene-oxide, and yields another and a less fusible modification, has been regarded as $3(CH_2O)$, but its integral weight is uncertain. When a solution of formaldehyde is digested with milk of lime it is changed into a sugar which has been named formose, represented by the general formula of the glucoses, $C_6H_{12}O_6 = 6(CH_2O)$. Indeed, by modifying the conditions of experiment many species of sugar, alike non-fermentescible and fermentescible, are obtained from formic aldehyde. From one of the latter, which has been designated acrose, and is a form of levulose, it has been found possible to produce anhydrous crystalline dextrose, and thus from the formic aldehyde itself to effect the synthesis of dextrose.[1]

§8. Other striking examples alike of isomerism and of polymerism are seen in many hydrocarbons, as in the terpenes, in acetylene and amylene; while the higher olefines are all polymers and possible homologues of the as yet unknown methylene CH_2. In the case of the terpenes proper we have a large number of distinct liquid and solid species differing alike in boiling point, in optical characteristics, and in various chemical relations, but having a common vapor-density corresponding to $C_{10}H_{16}$. These include (1) pinenes, which are liquids boiling at 156°–160° and having a specific gravity of about 0.876 at 0°; (2) citrenes; (3) sylvestrene; (4) terpilene; all liquids boiling from 170° to 176°

[1] Fischer: Ber. d. chem. Ges. **23**, 372, cited in This Journal **12**, 357–364.

and with specific gravities very near that of the pinenes; while the (5) camphenes are solid crystalline species. The various pinenes and citrenes are in great part broken up by heat into pentine, C_5H_8, which is again convertible into terpilene. The various terpenes are, moreover, easily polymerised, yielding denser and less volatile liquids, including sesquiterpenes, $C_{15}H_{24}$, and still higher polymers boiling at 300° and upwards. Acetylene, C_2H_2, under proper conditions of temperature, gives rise to a number of polymers, of which it suffices to mention benzene, $3(C_2H_2)$, cinnamene, $4(C_2H_2)$ (itself a liquid passing into a solid modification), and retene, $9(C_2H_2)$, a crystalline solid. Of the higher olefines, at least three are known as solids at ordinary temperatures, namely, octodecylene, $18(CH_2)$, cerotene, $27(CH_2)$, and melene, $30(CH_2)$, having melting-points of from 18° to 62° and specific gravities of 0.79, 0.86 and 0.89, respectively, water being 1.00. The integral or so-called molecular weight of these various hydrocarbons is known by the density of their vapors, as in the similar cases of the chlorides of carbon, silicon, aluminum and iron, and of the volatile oxides like those of carbon, arsenic, sulphur, selenium, ruthenium and osmium.

§9. By far the greater number of species, however, are either fixed at high temperatures or undergo heterogeneous decomposition thereby, and may be divided into two categories. First, those which are soluble in water or some other liquid, from which they can be recovered unaltered by change of temperature or by evaporation of the solvent. Such are the sugars and a vast number of non-volatile hydrocarbonaceous species, a great many chlorides, sulphates, phosphates, carbonates and other salts, as also the elementary solid species, sulphur, phosphorus and iodine. For these various bodies water, alcohol, ether, benzene, acetic acid, carbon disulphide and other solvents are familiarly employed. In the second category is included the great number of species which are altogether insoluble, or else are either decomposed, or enter into more or less stable combinations with their solvents. Such are the native silicates, oxides, carbonates and sulphides among compounds, and the various metals among elementary species.

§10. For these two categories of bodies it is obvious that the question of their integral or molecular weight must be approached by a wholly different process from that applied to volatile

bodies. Much attention has of late been given to the cryoscopic method of Raoult (with its modifications), which is applied for fixing this value for soluble non-volatile species, and depends upon the reduction of the temperature of congelation of the solvent which takes place after the solution therein of a known proportion of the solid species to be examined; the dissolving liquids chiefly used hitherto being water, acetic acid and benzene. The results obtained are approximative, and, moreover, are extremely instructive as illustrations of the subject now under consideration. Thus, Tollens and Mayer have deduced thereby for formaldehyde (obtained in aqueous solution by effecting the transformation of the insoluble formic paraldehyde by heating it in a sealed tube with water to near 140°) the numbers 34 and 35, the calculated integral or molecular weight being 30(= CH_2O). This solution, heated in a water-bath, regenerates the insoluble polymer, but evaporated over sulphuric acid gives a soft, soluble solid which, by Raoult's method, is found to correspond to 2(CH_2O). By applying this same method to dextrose, these observers found the number 188.7, the received formula for this and the other true glucoses being $C_6H_{12}O_6$(= 180); while arabinose and its isomer xylose, represented by $C_5H_{10}O_5$(= 150), give the numbers 155.1 and 154.1. For cane sugar and for lactose, which, with many other sugars, belong to the diglucosic type, designated as saccharose and represented by $C_{12}H_{22}O_{11}$(= 342), they found, by the method of Raoult, numbers which sustain this formula. For the sugar named raffinose, which occurs with saccharose in certain syrups, three formulas, with C_6, C_{12} and C_{18} respectively, have been proposed. The latter, making it a triglucosic sugar, is $C_{18}H_{32}O_{16}.5H_2O$(= 594), and experiments by the cryoscopic method gave numbers from 544 to 644, thus sustaining the triglucosic character, and showing at the same time that the range of error due to the necessary imperfections of the process is not inconsiderable.

§11. The recent application of this method to various uncrystalline amyloid bodies has given further results of great interest. The studies by many investigators of the hydrolysis of starch had already led to the conclusion that its constitution is far more complex than is indicated by the ancient formula $C_6H_{10}O_5$. The first action of cold dilute acids thereon changes it into the so-called soluble starch, which by hydrolysis is slowly converted into

amylodextrine, with the production of a portion of dextrose. The action of diastase, in like manner, by successive stages in hydrolysis gives rise to maltose and other forms of dextrine. By Raoult's method maltodextrine gives numbers closely approximating

$$C_{12}H_{22}O_{11} + (C_{12}H_{20}O_{10})_9 (= 990),$$

and amylodextrine,

$$C_{12}H_{22}O_{11} + (C_{12}H_{20}O_{10})_6 (= 2286);$$

inulin having a composition intermediate between the two. Raoult's method could not be applied to starch paste, but with soluble starch the depression in temperature produced, though slight, corresponded in a number of experiments to integral weights varying from 20,000 to 30,000. Messrs. Brown and Morris, to whom we owe these late investigations, are led to assign to soluble starch the formula

$$5(C_{12}H_{20}O_{10})_{20} (= 32{,}400),$$

thus multiplying the old empirical formula $C_6H_{10}O_5$ by 200. By the author's hypothesis, however, as restated in §5 of the present paper, the highest integral weights compatible with the observed specific gravities of starch and other amyloid bodies are approximately 32,000, and it therefore seems probable that the so-called soluble starch, which is apparently the first product of the depolymerisation of true starch, should be represented by some simple fraction, perhaps one-half the above, leading to an integral weight for soluble starch of 16,200. The above formula of Brown and Morris, equal to $200(C_6H_{10}O_5)$, will then represent starch itself, with an integral weight of 32,360 (O = 15.96) and a theoretical specific gravity of 1.509. The recent examination by Sabanéeff of glycogen by Raoult's method leads to the formula

$$(C_6H_{10}O_5)_{10} (= 1620).$$

§12. It will now be sufficiently evident that the values got by Raoult's method are not the integral or so-called molecular weights of the solid species themselves, or what we have designated *mineral species*, but of the *chemical species* which result from the depolymerisation of these, and which pass into solution. These values, moreover, bear no obvious relations to the specific gravities of these solid species, as appears when we compare sugars like xylose, dextrose, saccharose and raffinose with each other, and with the dextrines and soluble starch; bodies which with

such widely different integral weights in solution have almost identical specific gravities in the solid state. It is, in the language of the atomistic school, "the molecular mass" of the dissolved substance which we determine by Raoult's method, and not that of the solid or liquid mineral species, from the depolymerisation of which, in the process of solution, is derived the chemical species; the molecular or, in other words, the integral weight of which (H = 1) may vary widely in bodies nearly allied, as in hydrocarbons of identical centesimal constitution, different sugars, and certain amyloid substances. The total mineral condensation in such cases being essentially the same, the question is whether the depolymerisation or homogeneous disintegration which takes place in vaporisation or in solution shall resolve the mineral species into a greater or less number of chemical species.

Chemical species probably never assume liquid or solid forms. They are either vapors or gases, which by intrinsic condensation (polymerisation) pass into liquids or solids, or else, if their integral weight is too great to permit their existence in a gaseous condition at ordinary temperatures, unite with water, forming liquid hydrates, from which they separate, after a longer or shorter time, in solid or, more rarely, in liquid hydrated or anhydrous species. The appearance of such solid or liquid bodies in the midst of an aqueous solution marks the passage of the dissolved *chemical species* by polymerisation into a *mineral species;* a process often favored by mechanical agencies or by change of temperature.

§13. The significance of these relations is made more apparent by the writer's theory of solution, according to which there are formed in the process of aqueous solution definite compounds of the dissolved matters with water, accompanied with all the phenomena of chemical union; the further addition of water thereto giving rise either to new chemical arrangements of the substances present, or to simple admixtures of one definite solution or liquid species with another of unlike density. Examples of such admixtures of aqueous solutions are seen in the case of phenol and water, which when heated mix in all proportions, but on cooling separate into two layers, the lower a solution of phenol in water, and the upper a solution of water in phenol. Aniline and many other bodies present similar reactions with water below 100° C., and like results are got through the agency of pressure at still higher temperatures. Thus salicylic acid heated with water in a

sealed tube above 100° gives a solution which separates suddenly, on cooling to 91°, into two layers, each of which, according to Alexéeff,[1] grows turbid independently as cooling goes on. Similar separations of liquids have been noticed by Hannay and Hogarth in the case of alcoholic solutions of calcic chloride and ferric chloride, under pressure. Moreover, the spontaneous separation, long suspected, of many saline solutions into layers of unlike density through the influence of gravity, has been confirmed by the studies of Bodländer and the more recent ones of Traube and Neuberg. The conversion of denser solutions into solid hydrous species is in many cases but a question of temperature. Liquidity is only an accident of solution. Not only is all solution chemical union, but "all chemical union is nothing else than solution. The resulting species are, as it were, dissolved in each other, for solution is mutual." All precipitation and all crystallisation from solution thus involve chemical change, and all chemical species may theoretically exist in soluble states, from which they pass into polymeric mineral species, often insoluble.[2]

§14. A given chemical species, whether elementary or complex in constitution, may in some cases pass through two or more higher *chemical forms*, by successive condensations, until at last it assumes a *mineral form* as a liquid or a solid species, which in the latter case may either be colloidal or may take on a crystalline shape; the whole process, from the simplest chemical form, constituting an ascending series, in which the older and simpler forms are not lost but latent. It is to the converse of this process, or, in other words, to the depolymerisation by solution of solid mineral forms, that reference was had when, in 1853, the writer insisted upon "those chemical changes which commence only with the destruction of crystalline individuality," as quoted above in §4; or, in other words, to the breaking up of *mineral species* by solution into *chemical species*.

§15. The mineral form itself is, however, in many cases subject to other changes, since the solid species may undergo alterations in density, in hardness, in fusibility and in crystalline shape with-

[1] Bull. Soc. chim. II, **38**, 145.

[2] These views, set forth in 1853, and more fully in 1855, in Thoughts on Solution and the Chemical Process: Am. J. Sci. (II) **19**, 100-103, and Chemical Gazette for 1855, p. 92, are reinforced in the New Basis for Chemistry, pp. 98-99, and in The Theory of Solution: Brit. Assoc. Adv. Science, Sec. B, 1888; Chem. News **58**, 151. See also Mineral Physiology, etc., pp. 167-169. Similar views have since 1886 been put forward by Mendelèeff.

out passing by a process of fusion or solution. Thus, for example, of the many allotropic phases of solid sulphur we may designate three as the plastic amorphous or colloidal, the clinorhombic and the orthorhombic. Of these, the first two pass spontaneously after a time into the denser and more stable orthorhombic state, an alteration which, as Spring has shown, is accelerated by pressure. A still more striking case is found in tin, the gray brittle form of which, with a density of 5.8, by gentle heat, concussion or momentary pressure passes into the white malleable species with the density 7.3, and may again by considerable reduction of temperature revert to the lighter brittle species. So the orthorhombic calcium carbonate, aragonite, is, at a low red heat, transformed into the lighter rhombohedral form, calcite. Ice, moreover, at 0° passes by pressure into liquid water, with a considerable increase of density (as in the case of tin); the transformations of the two species being readily repeated by slight variations of temperature or of pressure. It would be easy to multiply instances of such changes of mineral form.

§16. In the case of insoluble non-volatile solids like tin and calcium carbonate we are precluded from the use alike of the vapor-density and the cryoscopic method as means of fixing the integral weight of the chemical species which by its polymerisation gives rise to the mineral species in question. We may add that even were the conditions such as to permit the application of either of these methods the presence of possible admixtures of different polymers might give rise to difficulties in their application, especially in cases where it is known that such polymers may have been simultaneously formed. Thus, for example, among the many polymers generated by the intrinsic condensation of acetylene, three, namely retene $(C_2H_2)_9$, cinnamene $(C_2H_2)_4$,—or rather its solid allotrope, metacinnamene—and benzene $(C_2H_2)_3$, are all solids at temperatures above 0°. An admixture of two or more of these might well have a fusing point which would tend to confound it with some intermediate species. Again, among the higher olefines, $(CH_2)_n$, three of which have been mentioned above (§8), octodecylene ($n = 18$), melts at 18° and has a density of 0.79; cerotene ($n = 27$) melts at 58° and has a density of 0.86; while melene ($n = 30$) melts at 62° and has a density of 0.89. Mixtures of any two of these would give rise to uncertainties like those which we have imagined in the case of the solid polymers

of acetylene. In both of these examples, it is true, separation of the intermingled hydrocarbons might be effected by differences in the solubility and the volatility of the polymeric species; but in other cases, where we have to deal with bodies alike non-volatile and insoluble, the problem becomes far more difficult. It is evident that, while in the case of gases and vapors the density varies directly as the integral weight of the chemical species, no such rule holds good in solids and liquids. This is well illustrated in the case of the three solid olefines just named, having, with small variations of density, integral weights for the chemical species which are to each other as 18 : 27 : 30, and also in that of the glucosic, diglucosic and triglucosic sugars, having for the chemical species integral weights nearly as 1 : 2 : 3, yet with specific gravities for the solid or mineral species which are almost identical.

§17. Among native mineral species there are not wanting instances of such mixtures, a good example being seen in the disulphide of iron, which constitutes alike the orthorhombic species marcasite, and the isometric species pyrite. Multiplied observations of specimens of the latter species by various skilled naturalists show that its specific gravity may vary from 4.80 to 5.00 and even 5.15 and 5.20 for well-defined pyritohedral crystals. On the other hand, marcasite itself may vary in specific gravity from 4.75 to about 5.00 (4.987), with a hardness on the scale of Mohs of 6.0–6.5; while the denser isometric species attains 6.5–7.0. The latter strikes fire strongly with steel, giving a faint sulphurous odor; marcasite, on the contrary, feebly, giving a strong odor. Differences in color and texture also distinguish the denser from the lighter sulphide. A. A. Julien, who has lately examined this question with great care, concludes that we have in these minerals of intermediate density an intermingling of two disulphides of unlike degrees of condensation. Each of these species would thus be dimorphous and might include admixtures of the other.[1] It is difficult to conceive any other explanation of these facts, which are precisely what we should expect in the case of admixtures of polymeric bodies like the hydrocarbons noted above. It will be found that an admixture of three parts of a disulphide of iron, sp. gr. 5.18, and two parts of one of sp. gr. 4.75, would give a mean sp. gr. of 5.00, which is that assigned by many

[1] A. A. Julien, N. Y. Acad. Sci. 1886, 1887, Vol. 3, No. 12, 4, Nos. 3, 5, 6, 7.

observers to pyrite, and very near the maximum specific gravity of marcasite.

Similar differences in density are met with among the orthorhombic and isometric arsenides of cobalt, nickel and iron, represented by the general formula MAs_2, as shown in safflorite and smaltite, verified by the recent studies of MacCay. Another example of the kind, uncomplicated by the question of dimorphism, is seen in sodium chloride. Several careful observers concur in giving for specimens of this substance at ordinary temperatures a sp. gr. of about 2.25 (2.20, 2.23, 2.26); and others, apparently equally worthy of confidence, have found about 2.00 (2.01, 2.03, 2.06, 2.08), while the greater number of observations range from 2.14 to 2.20. These wide variations in density in such a familiar species are the more remarkable for the reason that the chlorides of potassium and ammonium present no such notable variations. A similar condition of things is apparent in crystals of zircon, and many other cases might be cited showing that we have, as in the case of the iron disulphides, variable admixtures of two mineral species with the same centesimal composition but of unlike condensation.

§18. It will now be apparent that we have to deal with processes of condensation belonging alike to chemical species and to mineral species. Thus, for example, with acetylene, pentine and their polymers, we have in each case chemical species having a common centesimal composition with widely different co-efficients of chemical condensation, as is apparent when we compare their vapor-densities; which, moreover, present no simple or apparent relations to their specific gravities in the liquid or solid state. We may recall in this connection the already cited case of formaldehyde, of which the equivalent weight is fixed by its vapor-density as well as by Raoult's method, with those of xylose, glucose and the related sugars and amyloid bodies; species for which the chemical condensation presents a very wide range. In these cases we are enabled by vapor-density, by the cryoscopic method, or else by direct chemical analysis, to determine the minimum value of the chemical integer, and in this latter way we are led to assign in many cases very elevated numbers, as seen in such compounds as the cobalt amine salts and the polytungstates, the simplest admissible formulas of which give integral weights of thousands or tens of thousands.

§19. The history of the development of this modern conception in chemistry is one of such importance as to demand a somewhat extended study. The earliest statement, so far as the writer is aware, of the application of the doctrine of complex formulas, of high equivalent weights, and of homologous relations (already recognised among hydrocarbonaceous bodies in the domain of organic chemistry), to mineral, or inorganic, chemistry will be found in a paper by him in 1853. Therein it was contended that isomorphous solid species, at least, "have the same equivalent volume, so that their equivalent weights (as in the case of vapors) are directly as their densities; and the equivalents of mineral species are as much more elevated than those of the carbon series as their specific gravities are higher." Referring to the latter, "the hydrocarbonaceous, or so-called organic, species," and to the law of progressive or homologous series therein first pointed out by James Schiel, of St. Louis, and soon after adopted by Charles Gerhardt, it was said that "it may be expected that mineral species will exhibit the same general relations as those of the carbon series, and the principle of homology be greatly extended in its application. The history of mineral species affords many instances of isomorphous silicates, whose formulas differ by $n(O_2M_2)$, as the tourmalines, and the silicates of alumina and of magnesia."

It was then further declared that the native mineral carbonates or carbon-spars must be represented as polycarbonates having not less than from "twelve to eighteen equivalents of base replaceable so as to give rise to a great number of species"; among which the relations of their densities were said to "indicate the existence of several homologous genera which are isomorphous." In subsequent papers, in 1853 and 1854, attempts were made to show that in these polycarbonates, $n(CMO_3)$, the different values of n might be not less than 22, 25, 30, 36 and 40. Similar elevated formulas were also given in 1853 for various polysilicates, as in the cases of augite, amphibole and wollastonite, and of the feldspars, albite, anorthite and orthoclase. In this connection the complex silicates containing chlorides, carbonates and sulphates were considered and compared to basic salts.[1]

[1] "Theory of Chemical Changes and Equivalent Volumes," Am. J. Sci. **15**, 226–234; Phil. Mag. (4), **5**, 526, and in a German translation in the Chem. Centralblatt of Leipsic for the same year (p. 849); also in the author's "Chem. and Geol. Essays," pp. 427–437. Further, "The Constitution and Equivalent Volume of Mineral Species," Am. J. Sci. **16**, 203–218, and,

The variations in the ratios of silica and alumina in nearly related species, and the apparent partial replacement therein of silica by the latter, then imperfectly understood, were noted in 1854 as seeming to invalidate the distinction between silica, as the negative or acidic member, and the positive or basylous member of these oxidised compounds, in which alumina was at that time still included.

§20. These views of polymerism in mineral species, involving on the one hand the conception of many equivalents of replaceable base, and on the other of many equivalents of the acidic or negative element, which might be either carbonic, silicic or boric oxide, or might include with the latter alumina, sulphates, carbonates or fluorides, though thus enunciated in 1853, found no favor among chemists until 1860, when Adolphe Wurtz again put forth the notion of polysilicates, citing in connection therewith the metastannates of Frémy, in which the negative element consists of $5(SnO_2)$. The similar metatungstates or tetratungstates, the pyroborates, the polyphosphates of Fleitmann and Henneberg, including tetraphosphates and dekaphosphates, and the not less complex phosphates of Wallroth, with $9(P_2O_5)$, soon showed that such a polymerism is not exceptional in negative or acidic oxides. The studies of other chemists, moreover, made it known that similar compounds, including different negative oxides of the same or of unlike valencies, were not less frequent; as appears in the complex phosphovanadates and arsenovanadates, in the aluminomolybdates, the ferrimolybdates, the borotungstates, the silicotungstates, the phosphotungstates, the phosphomolybdates, the stannophosphomolybdates, and salts of still greater complexity and of very high equivalent; often presenting series which illustrate in a striking manner the extension to such mineral species of the law of progressive series.

The high integral weight, the limited basicity and the partial instability of these complex salts are well illustrated in the phosphomolybdate of ammonia formed in the ordinary method for determining phosphorus thereby. This insoluble compound, when precipitated in presence of an excess of chlorhydric or nitric acid,

in abstract, in the author's "Chem. and Geol. Essays," p. 438, etc. Also, "Illustrations of Chemical Homology," Proc. Am. Asso. Adv. Sci. 1854, pp. 237–247; also, in abstract, Am. J. Sci. for September of the same year; and noticed, with extracts, in the author's "Chem. and Geol. Essays," p. 438 et seq. The whole question is further discussed in the author's "Mineral Physiology, etc.," pp. 283–295.

contains $12MoO_3.PO_4.(NH_4)_2$, besides $2NO_3.H_2O$ or $2HCl.H_2O$, constituting a nitro-, or a chlorhydro-, phosphododekamolybdate; but by desiccation at 150° these volatile acids and water are expelled, leaving the phosphomolybdate with 3.78 per cent. of phosphoric oxide, P_2O_5.

§21. We have thus endeavored to trace the steps by which, from the writer's first enunciation, in 1853, of complex formulas, high integral weights, and homologous, or progressive, series in mineral species, chemists have been led up to the comprehensive generalisation which Wolcott Gibbs has embodied in the important conception of what he has called complex inorganic acids. The results of chemical analysis, while they permit us in many instances to assign small integral weights to chemical species, force us to conclude that in other instances these integral weights are very elevated, conclusions which in the one and in the other case are confirmed alike by the vapor-density and by the cryoscopic method; which latter it will be desirable to verify still further by the study of many soluble salts of apparently complex constitution.

§22. The cases which we have just considered show in chemical species of related centesimal composition, as in formaldehyde, xylose, glucose, the higher sugars, the dextrines and soluble starch, integral weights rising from 30, 150 and 180 to numbers which cannot be less than thousands. These figures suggest for chemical species a range of integral weights which may conceivably rise to that of the mineral species itself. Instead of being, as in glucose and other sugars, a multiple of the chemical integer by a high number, the co-efficient for the mineral species becomes a small one, as in the case of the dextrines and soluble starch, or of the cobaltamines and the polytungstates. So far as is yet known, however, there intervenes, in all cases, a greater or less polymerisation, the study of which will be found to have important thermo-chemical relations.

If we consider the four groups of sugars represented chemically by xylose and arabinose (C_5), glucose (C_6), saccharose (C_{12}), and raffinose (C_{18}), but having for the mineral species essentially the same specific gravity, assumed to be 1.5, we shall have for the co-efficients of the mineral species, respectively, the numbers 214, 180, 94 and 54, corresponding to a common integral weight therefor of 32,100; xylose being $214(C_5H_{10}O_5)$, glucose $180(C_6H_{12}O_6)$, etc. In the case of the volatile polymeric hydrocarbons already

mentioned (§8), octodecylene $(CH_2)_{18}$, cerotene $(CH_2)_{27}$, and melene $(CH_2)_{30}$, assuming the specific gravities assigned for the solids, namely 0.79, 0.86 and 0.89, to be correct, we have respectively the co-efficients for the solid mineral species of 67, 48 and 45. Melene will be $45(CH_2)_{20}$, cerotene $48(CH_2)_{27}$, and octodecylene $67(CH_2)_{18}$.

§23. The ammonio-cobalt salts, from the results of chemical analysis, have necessarily high integral weights for the chemical species, and have assigned to them densities of about 1.7–1.8; the former figure corresponding to an integral weight for the mineral species of about 36,380.[1] The minimum chemical weight for the orthometaphosphate of luteocobalt (= 2540) would demand a co-efficient for the mineral species of 14, since $14 \times 2540 = 35{,}580$. In like manner the soluble crystalline hydrous polyphosphotungstates have for sodium salts, according to Scheibler, specific gravities of 3.84–3.98, and for a barium salt 4.3. I find no determination of specific gravity for the highly complex polyphosphovanadate (§1) to which Gibbs assigns a chemical weight of 20,058, and which, should its co-efficient of polymerisation be 4, would have a specific gravity of 3.75, nearly. More or less uncertainty must, however, still exist with regard to the true chemical formulas, and consequently to the integral weights of chemical species of such complex constitution as those now under consideration. Under the name of tungsten-bronzes have been conveniently included several anhydrous crystalline bodies, metallic in luster, conductors of electricity and highly electro-negative, which are nevertheless oxidised compounds of tungsten and an alkali-metal. The tungsten-bronze first described by Wöhler is, in the opinion of Gibbs, probably $16WO_3.4WO_3.7Na_2O$ (= 5002). To this has been assigned a specific gravity of 6.617; to another sodium species, 7.28; and to a potassium species, 7.60.

§24. The fact that in the soluble hydrous polytungstates, hydrocarbon radicles like methyl, ethyl and phenyl, may enter, helps to break down the barrier, not yet wholly removed, which once separated the so-called organic and inorganic compounds (§2). Even the stability of insoluble silicates is not proof against similar changes,

[1] The revision by Crafts in 1888 of Regnault's determination of the weight of a liter of hydrogen in the latitude of Paris, making it 0.08988 gram (instead of 0.08975 gram) gives—if O = 15.96—for the integral weight of water 21,335 in place of 21,406. In the uncertainty which still prevails as to the precise value of oxygen as compared with hydrogen, we may yet retain for water—the unit of specific gravity for liquids and solids—the number hitherto adopted, 21,400, as a close approximation, since the difference would only involve an error of about three-thousandths of a unit in such specific gravities.

as shown in the case of artificial ultramarine. This, which is got as a blue, green or violet crystalline powder, appears to be essentially a peculiar sodium aluminosilicate in which the oxygen is partially replaced by sulphur. By digestion with a solution of silver nitrate a yellow substance is got in which silver replaces sodium, and this with ethyl iodide yields a compound into which the alcohol radicle enters, and which by subsequent treatment with sodium chloride gives off ethyl chloride and regenerates blue ultramarine. The silver in the yellow species may also be replaced by potassium or by lithium, the last giving also a blue ultramarine. Similar compounds are obtained from ultramarine with the iodides of amyl, allyl, and benzyl.[1] It is probable that only their great insolubility prevents us from getting somewhat similar results with more highly condensed silicates, such as the feldspars, micas and tourmalines.

§25. It will be clear to those who have followed the preceding argument, that in cases where neither the vapor-density nor the cryoscopic method can be invoked, that is to say in non-volatile and insoluble mineral species, we have not the means of determining the integral weight of the chemical species which by its subsequent condensation generates such mineral species; or of discovering whether this may have attained that condensation by a single step or by successive stages. Thus, by hypothesis, a solid like retene might be generated directly by the intrinsic condensation of acetylene, or from benzene; the production of the latter hydrocarbon marking an intermediate stage in the progress of homogeneous integration. What stages, if any, intervene in the passage from the soluble normal calcium carbonate to the insoluble crystalline mineral species, calcite and aragonite, we may never know, though from the existence of these two mineral species of identical centesimal composition with different degrees of condensation and of solubility in acids, corresponding to the differences observed in the various polymers of many hydrocarbons, aldehydes, etc., we may with great probability suspect the existence of intermediate and unstable stages of condensation in calcium carbonate. The same argument applies equally to the unlike forms of silicon dioxide, tridymite and quartz, differing alike in specific gravity and in solubility; to the two forms of iron disulphide; and to other cases too many to recall.

[1] For a summary of the results of the study of ultramarine by Neumann, Philipp and de Forcrand, see Watts, Dict. Chem., 3d. Suppl., 2069-2071.

§26. We can in very many cases recognise at least two distinct stages of polymerisation in the passage of a given chemical species, either simple or compound, into a mineral species. The first stage is seen when the vapor of sulphur (S_8) passes by intrinsic condensation into the denser vapor (S_6); gaseous acetylene into the vapor of benzene, of cinnamene, or of retene; or when formaldehyde dissolved in water is changed to an aqueous solution of formose. The second stage is seen in the passage of the dense sulphur vapor, the polymerised hydrocarbon vapors, or the dissolved formose, into liquid or solid forms. For the great multitude of mineral species of which the corresponding volatile or soluble species are unknown to us, the means of marking these separate stages are wanting, and we have but two data: the specific gravity of the mineral species, water being unity, and the equivalent weight as deduced from the results of chemical analysis; $d =$ the specific gravity and $p =$ the equivalent weight. The latter, for compound species, may be calculated from the simplest formula which represents intelligibly the results of such analysis, or—as we have elsewhere proposed as the basis of a wider comparison which should include all metallic oxides, salts and haloid compounds—by the adoption for p of a still simpler and an arbitrary unit. For all such species "we assume as the unit for p a weight including that of $H = 1$, of $Cl = 35.5$, or of $O \div 2 = 8$. By thus adopting a combining weight of 8.0 for oxygen, we get a unit which gives a common term of comparison for oxides, sulphides, chlorides, fluorides, and for intermediate compounds like the oxysulphides and oxyfluorides common in native species." For all silicates, carbonates, sulphates, phosphates, and more complex species, we find the value for p "by dividing in all cases the empirical equivalent weight by twice the number of oxygen portions ($O = 16$) *plus* the number of chlorine or fluorine portions."[1] This method was already adopted by the author in 1886, and he has since proposed to complete it by the device of a notation as near as may be monadic, in which, by the use of various kinds of type, the valencies of the combining elements are made apparent.[2]

[1] For a further discussion of this question see the author on Chemical Integration in Am. J. Sci. for August, and in Chem. News **56**, 136, 149; also his volume, "A New Basis for Chemistry," 1888, 2d ed., pp. 225-227, and a French translation thereof by Prof. W. Spring, with additions by the author, entitled "Un Système Chimique Nouveau," Paris, 1889.

[2] See in the author's "Mineral Physiology and Physiography" an essay on A Natural System of Mineralogy, with a Classification of Silicates; and later, Notes on Valency, Basicity, Complex Acids and Chemical Notation: Chem. News **61**, 267.

§27. Since the arbitrary mean chemical unit $\not{p}$, thus assumed, represents in all cases an aliquot part of the chemical species, however simple or however complex, which by its final intrinsic condensation has generated the mineral species whose specific gravity ($= d$) is known, it follows that the equation $\not{p} \div d = v$, giving in v the reciprocal of the co-efficient of condensation, permits a ready comparison of the relative condensation in mineral species, upon which, as we have elsewhere endeavored to show, the hardness and the chemical indifference of solids depend.

It will be remembered that $\not{p}$, which represents the equivalent weight of the chemical unit, corresponds in the last analysis to the specific gravity of that unit, presumed to be gaseous—hydrogen gas at standard temperature and pressure being unity ($H = 1$)—while d represents the specific gravity of the liquid or solid mineral species, liquid water at its point of condensation at standard pressure being unity ($1 = 21{,}400$). The value deduced from this conventional $\not{p}$ is readily adapted to any rational formula which may be admitted for the species in question. Thus quartz, represented as silicon dioxide, $SiO_2 = 60 \div 4 = 15 = \not{p}$, and this being divided by 2.65, the specific gravity of quartz, we find $v = 5.66$, which for SiO_2 gives $v = 22.64$. We have then the proportion

$$22.64 : 21{,}400 :: 1 : 945.$$

In other words, if simple silicon dioxide passes directly into the mineral species quartz, the co-efficient of condensation is approximately 945 or perhaps $950(SiO_2)$. Should it be found, as is probable, that silicon dioxide in its soluble colloidal condition is a polymer of greater or less equivalent weight, represented by $(SiO_2)_{10}$ or by $(SiO_2)_{50}$, the above co-efficient therefor would be divided by these numbers; the total co-efficient of mineral condensation, comprising two or even more stages, being in each case the same. In the application of Raoult's method to colloidal silica, the reduction of the freezing point, according to Sabanéeff, was so slight that the values all came within the limits of errors of observation,[1] as would also appear to be the case with soluble starch.

To take another example, calcite, $CCaO_3 = 100 \div 6 = 16.66 = \not{p}$. Dividing $\not{p}$ by 2.73, as the specific gravity of calcite, we find $v = 6.10$ nearly, which for $CCaO_3$ gives $v = 36.6$,

$$36.6 : 21{,}400 :: 1 : 584.$$

[1] Am. J. Sci. (III), **40**, 87.

The condensation from $CCaO_3$ to calcite of specific gravity 2.73, is thus represented by $584(CCaO_3)$. Here, too, as in the case of silicon dioxide, it is probable that there exists an intermediate polymer, represented by a soluble form of carbonate of lime, long since noticed by the writer.[1]

§28. These numbers thus arrived at for quartz and for calcite are, of course, but approximations, since the exact equivalent weights of oxygen and of silicon are still uncertain, and since, moreover, there are small variations in the specific gravity of the mineral species themselves, from which Breithaupt with much plausibility conjectured, in the case of calcite, the existence of several species, rhombohedral in form, with specific gravities ranging from 2.652 to 2.754. At the same time we must not overlook the calcium carbonate, aragonite, harder and less soluble in acids, with a specific gravity of 2.94, showing a higher intrinsic condensation than any calcite.

We have spoken of the views advanced in this paper as based on an hypothesis. It is, however, an hypothesis founded on a belief in the universality and the invariability of the law of volumes, and one which appears to be in complete harmony with the facts of chemistry so far observed. As one of the conclusions of a lifetime devoted to the study of certain chemical problems discussed more at length in the later editions of his New Basis for Chemistry, the writer now submits his paper to the judgment of philosophers.

NEW YORK, *September*, 1890.

[1] Recently-precipitated and still gelatinous calcium carbonate is soluble in water containing small quantities of calcium chloride or of magnesium sulphate, a liter at ordinary temperatures holding for many hours a gram or more of the dissolved carbonate, which, however, finally separates completely in transparent hydrated crystals, $CCaO_3.5H_2O$. See the History of Lime and Magnesia Salts, Am. J. Sci. 1866, (2) **13**, 58, 59; also Mineral Physiology, etc., p. 168.

REVIEWS AND REPORTS.

THE ELEMENTS OF CRYSTALLOGRAPHY FOR STUDENTS OF CHEMISTRY, PHYSICS AND MINERALOGY. By G. H. WILLIAMS, Ph. D. Pp. viii + 250, with 383 Figs. New York: Holt & Co., 1890.

A concise statement of the principles of crystallography has long been needed by the chemist who is interested in the study of the internal structure of the substances with which he is daily in contact. The logical treatment of crystallography by Dr. Groth, in his treatise so well known under its title "Physikalische Krystallographie" (Leipzig, 1885), has rendered it one of the most valuable aids to that branch of chemists engaged in the solution of the problem with relation to the arrangement of molecules in space and of the atoms in the molecule.

The author of the present volume, largely based upon that of Groth, has sought not only to introduce the beautiful logic of the German crystallographer to English-reading students, but he has also attempted to simplify the discussion of crystal forms so that it may be grasped by the busy chemist and the young college man, and at the same time prove of value to the mineralogist. The result of his labors is a book that contains all of the fundamental truths established by the study of crystals, so stated that they are easily understood. Beginning with the explanation of the differences between chemical molecules and crystal particles, the book carries the reader through the seven crystallographic systems, introduces him to crystal aggregates, describes to him the causes of the imperfections in crystals, and finally gives him about thirty pages of hints on the projection and construction of crystal figures. Throughout the entire volume emphasis is laid upon the fact that the crystal forms are functions of chemical composition, and symmetry is made the basis of the discussion of the crystal forms.

The author deserves the thanks not only of English-reading students for giving them the first clear English exposition of the science which is the subject of his work, but he deserves as well the thanks of French and German chemists and physicists for sifting from the ponderous volumes of the German crystallographers their essential portions and incorporating them in such a convenient form. The publishers, also, are to be congratulated on their success in accomplishing such a difficult undertaking as was the publication of this little volume with its many unusual symbols and crystallographic figures. The book should receive a hearty welcome from every chemist as well as from every mineralogist.

W. S. B.

Hydrazoic Acid.

Dr. Theodor Curtius, of Munich, has obtained a new gaseous compound of nitrogen and hydrogen, and has described its properties in an address made in the chemical section of the recent German Scientific Congress at Bremen. Neither this address nor any article by the author has yet reached us; from an article in *Nature* we abstract a brief preliminary notice.

The gas has the composition HN_3, and Curtius gives it the constitution H—N—N, proving it to be the hydrogen compound

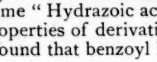
corresponding to the diazo-benzene-imide of Griess, C_6H_5—N—N.

The gas dissolves in water with great avidity, forming a solution which possesses strongly acid properties, and dissolves many metals such as iron, copper and zinc, with evolution of hydrogen and formation of nitrides, the metal replacing the hydrogen. Curtius names this gas "Stickstoff-wasserstoffsaüre." As English equivalent the name "Hydrazoic acid" is proposed.

In studying the properties of derivatives of hydrazine hydrate N_2H_4, H_2O, Curtius found that benzoyl hydrazine,

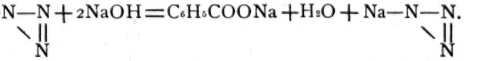
$$C_6H_5—CO—NH—NH_2,$$

when treated with nitrous acid forms a nitroso compound,



which spontaneously changes, losing water, into benzoyl-azo-imide $C_6H_5—CO—N—N$; benzoyl-azo-imide saponified with

alkali yields the alkaline salt of the new acid,



On warming this sodium salt with dilute sulphuric acid, H–N–N

is liberated as a gas of fearfully penetrating odor, causing catarrh. Hot concentrated sulphuric acid decomposes the gaseous hydrazoic acid. The solution of the gaseous acid in water strongly resembles aqueous hydrochloric acid; on distillation a concentrated acid first passes over, and afterwards a more dilute acid of constant composition. The aqueous solution has the odor of the free gas and is strongly acid to litmus. With ammonia gas, hydrazoic acid gas forms dense white fumes of the ammonium salt N_4H_4, or NH_4—N—N, a compound completely volatile below

100°, and crystallising, but not in forms of the regular system. The silver and mercurous salts are insoluble in water, the other salts are readily soluble. The barium salt, BaN_6, crystallises from the solution in large brilliant anhydrous crystals. The silver salt, $Ag—N—N$, strongly resembles silver chloride, but

$$\begin{array}{l} \diagdown \\ \quad N \end{array} \!\!\parallel$$

does not darken when exposed to light. It has fearfully explosive properties; one milligram of this salt, placed on an iron plate and touched with a heated glass rod, exploded with a loud detonation, distorting the plate. The mercurous salt is also explosive. The metallic salts are readily converted into ethereal salts when treated with haloid ethers. The phenyl salt thus prepared, $C_6H_5—N—N$, is in every way identical with the diazo-benzene-

$$\begin{array}{l} \diagdown \\ \quad N \end{array} \!\!\parallel$$

imide of Griess.

E. Renouf.

OBITUARY.

Silas H. Douglas died in Ann Arbor, Mich., August 26, 1890, at the age of seventy-four. He had been Professor of Chemistry in the University of Michigan from 1846 to 1877. The chemical laboratory of that institution, erected in 1856 and repeatedly extended, was the result of his labors, continued with energy through the active portion of his life. For a number of years his health had been infirm and he had remained in the retirement of his devoted family.

Professor Heinrich Will, the successor of Liebig at Giessen, died October 15, 1890. In the first rank among teachers of chemistry, he occupied a most enviable position. The many congratulatory letters received from all parts of the world on the occasion of the fiftieth anniversary of the date on which he received his degree, testify to the high reputation he had won for himself among chemists. Will is best known outside of Germany through his great work upon Chemical Analysis, and his editorship during many years of the *Jahresbericht*. He was a prominent figure in that distinguished group of the pupils of Liebig, of whom Kopp, Fresenius, v. Hofmann, and v. Pettenkofer still remain.